

Figure 1. Structure of 1-*n*-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆].

Experimental Section

The ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆], was purchased from Sachem and contained less than 3 ppm residual chloride. It was dried and degassed under vacuum at room temperature for several days prior to use. Karl Fischer analysis of the [bmim][PF₆] purchased from Sachem subjected to this procedure resulted in approximately 0.18 wt % residual water, which we consider to be satisfactory for these experiments. Drying and degassing is extremely important as the IL will uptake several weight percent of water when left open to the atmosphere for several hours (measurements from our laboratory). The small amount of water impurity has a dramatic effect on the phase behavior of the IL.⁶ Hexane and benzene were chosen as the roots to which numerous substituent groups were added to explore the effect of chemical structure on the solubility and extractability of an organic solute in and from an IL.

Solubility studies of the organics in the [bmim][PF₆] ionic liquid were carried out under ambient conditions, 22 ± 0.2 °C and 0.98 ± 0.03 bar. The IL-solute mixtures were stirred vigorously in closed containers under ambient conditions to avoid recontamination with air and water vapor and for several hours to ensure equilibrium. The contact time with air for all of the samples was on the order of just a few minutes, after which they were sealed in vials containing a small vapor space. Our experience is that this short contact time will not result in any significant water absorption. Several of the organics exhibited immiscibility with the IL, as observed by the formation of two liquid phases. For the organics exhibiting strong absorption in the UV-vis range, UV-vis spectroscopy and Beer's Law were used to determine the concentration of the organic-saturated [bmim][PF₆] phase. For these investigations, no attempts were made to analyze the organic-rich phase, although we anticipate that [bmim][PF₆] will dissolve to some extent in these liquid organics. Solubilities of the organics not absorbing in the UV-vis range were determined by gravimetric analysis. The organic solute was added to the IL dropwise until the first sign of a second liquid phase was observed. For those compounds found to be completely miscible with [bmim][PF₆], this refers to complete miscibility over the entire composition range. This was ascertained by adding up to five times the weight of organic to the IL dropwise without the formation of a second liquid phase ever being observed. The method of analysis and associated UV-vis wavelengths are listed in Table 1. There have been some qualitative solubility measurements for organic solutes in [bmim][PF₆], including determinations of the number of phases observed for 50/50 wt % solutions of [bmim][PF₆] and [bmim][BF₄] with methanol, ethanol, and unidentified hydrocarbons⁷ and the solubilities of some cyclodextrins and macrocyclic antibiotics.⁸ However, to

our knowledge, these are the first quantitative measurements of the solubilities of a systematic group of organic compounds in [bmim][PF₆] to be reported in the literature.

Extraction experiments were performed with an ISCO 220SX high-pressure extraction apparatus. All experiments were carried out at 40 ± 1 °C and 138 ± 0.2 bar. Extraction of the pure [bmim][PF₆] using SCCO₂ was first investigated with UV-vis analysis, verifying the lack of IL in the CO₂ phase.⁵ [bmim][PF₆] was doped with each organic solute, well below the solubility limit, and then loaded into a high-pressure cartridge filled with glass beads. The cartridge was then pressurized with CO₂ and allowed sufficient time, approximately 40 min, for equilibration. A small volume of the solute-saturated CO₂ phase was depressurized through a heated restrictor and collected in a flask of ethanol. The collected solution was then scanned on a UV-vis spectrophotometer, which allowed for the quantitative calculation of the amount of solute extracted. Each subsequent sample was collected in a fresh flask of ethanol with the amount extracted added to the previous sample, generating the extraction curves of Figures 2 and 3. For the solutes not exhibiting peaks in the UV-vis region, the extraction analysis was performed gravimetrically. Again, the saturated CO₂ stream was depressurized and collected in a cooled empty flask for weighing. When the solute appeared to have reached the extraction limit, the cartridge within the extraction unit was depressurized and weighed. Because no IL is extracted from the cartridge, the change in weight upon depressurization reflected the amount of organic solute extracted. In all cases, the results obtained agreed with the amounts determined from the extraction samples to within 3%.

Results

Solubility Measurements. The solubilities of 20 different solid and liquid compounds in [bmim][PF₆] were measured at 22 °C and ambient pressure (0.98 ± 0.03 bar) and are summarized in Table 1. Benzene and hexane were chosen to represent two basic families, aromatics and aliphatics. Numerous substituent groups were added to benzene and hexane in an effort to explore any possible effect chemical structure might have on solubility in and recovery from the [bmim][PF₆] ionic liquid. The substituent groups represented are halogen, alcohol, ether, amine, ketone, carboxylic acid, ester, amide, and aldehyde. These compounds represent a wide range of polarity, from nonpolar to a dipole moment of 3.9 D. The charge states of the solutes when they are dissolved in the ionic liquid are not known. It is possible that some compounds, like benzoic acid, might be partially dissociated in solution.

Organics with the potential for strong intermolecular interactions, those with a large dipole moment for example, generally exhibited complete miscibility or a large degree of solubility in [bmim][PF₆]. With the exception of benzene and chlorobenzene, compounds that clearly exhibited liquid-liquid phase equilibria, all of the liquid organics within the benzene family were completely miscible with [bmim][PF₆], whereas the hexane counterparts were generally immiscible. By immiscible, we mean that, in some proportions, the binary mixtures formed two liquid phases. The phases are not pure—they exhibit substantial mutual solubility. In other words, substantial amounts of the organic

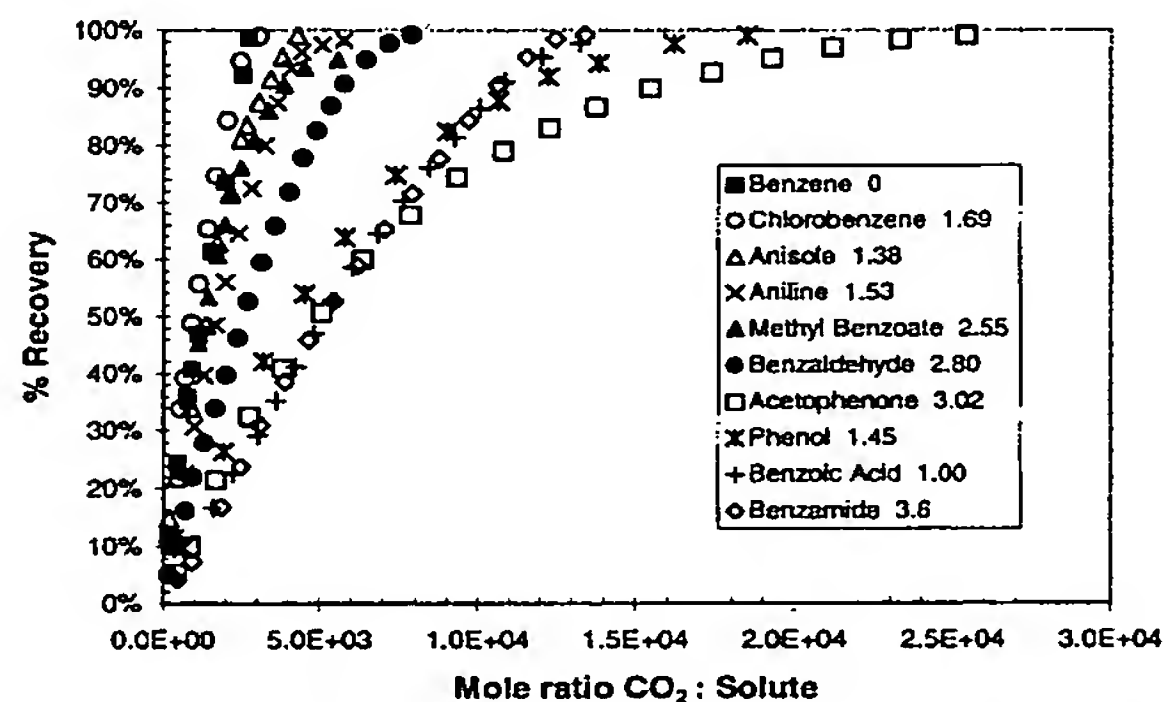
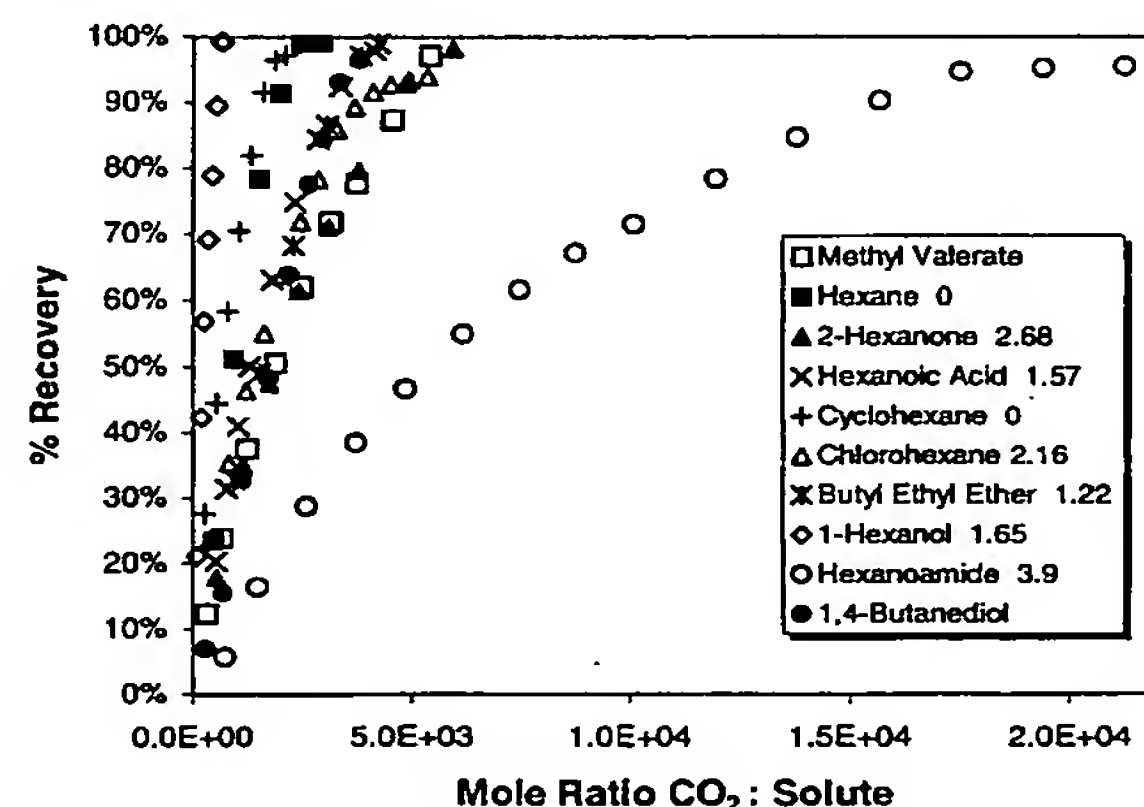
Table 1. Organic Solute Solubilities in [bmim][PF₆] at *T* = 22 °C, along with Solute Dipole Moments, Melting Temperatures, and Normal Boiling Temperatures^a

solute ^a	solubility (solute mole fraction)	dipole moment (Debye)	analysis method (wavelength (nm))	<i>T_m</i> (°C)	<i>T_b</i> (°C)
benzene	0.66	0	UV-vis (255, 261)	5.5	80
chlorobenzene (s) (halogen)	0.58	1.69	UV-vis (258, 271)	-45	132
phenol (alcohol)	0.69	1.45	UV-vis (273)	40	182
anisole (ether)	miscible	1.38	UV-vis (271, 278)	-37	154
aniline (amine)	miscible	1.53	UV-vis (236, 286)	-6	184
acetophenone (ketone)	miscible	3.02	UV-vis (241)	19	202
benzoic acid (s) (carboxylic acid)	0.07	1.00	UV-vis (231)	121	249
methyl benzoate (ester)	miscible	2.55	UV-vis (273)	-12	198
benzamide (s) (amide)	0.04	3.60	UV-vis (225)	128	288
benzaldehyde (aldehyde)	miscible	2.80	UV-vis (245)	-26	178
hexane	miscible	0	gravimetric	-95	69
1-chlorohexane (halogen)	0.25	1.99	gravimetric	-94	133
1-hexanol (alcohol)	0.26	1.65	gravimetric	-52	156
butyl ethyl ether (ether)	0.06	1.22	gravimetric	-124	91
cyclohexane	0.21	0	gravimetric	6.5	81
2-hexanone (ketone)	miscible	2.68	UV-vis (278)	-57	127
hexanoic acid (carboxylic acid)	0.13	1.57	UV-vis (219)	-3	202
methyl pentanoate (ester)	0.59		UV-vis (209)		128
hexanamide (s) (amide)	0.06	3.90	UV-vis (203)	100	225
1,4-butanediol	0.51	2.58	gravimetric	16	230

^a Solids are indicated by (s).

dissolve in the "IL-rich" phase, and the IL dissolves in the "organic-rich" phase. For example, the ether pair, anisole and butyl ethyl ether, have similar dipole moments, 1.38 and 1.22 D, but differ significantly in solubility as anisole is miscible with [bmim][PF₆] and butyl ethyl ether dissolves in the IL only for a mole fraction of 0.06. Only two liquids from the aliphatic hexane family were completely miscible with [bmim][PF₆] over the whole composition range, hexane and 2-hexanone. Solubilities of the solid organic solutes, with the exception of phenol, were considerably less than those of the liquid organics. Overall, the solubilities of the benzene-based organics were significantly greater than those of their hexane-based counterparts.

Extraction Studies. The primary goal of this work was to explore the feasibility of using SCCO₂ to recover organic solutes dissolved in an ionic liquid. [bmim][PF₆] was doped with 20 organic solutes not only to determine the extent of solute recovery from the IL but also to explore possible trends regarding the amount of CO₂ necessary for extraction. 1,4-Butanediol has been included in this investigation as an example of a high-boiling-point organic liquid for which separation via distillation is not a reasonable option. All organic solutes exhibited a greater than 95% recovery, a clear indication that, although the ionic nature of the IL might lead to an interaction with a solute, it does not limit the extent of extraction. SCCO₂ extraction achieved greater than 98% solute recovery for several of the organics before the extraction tests were terminated. Extraction of the benzene-based solutes from [bmim][PF₆] with SCCO₂ is illustrated in Figure 2. To normalize the results for the different solute amounts loaded into the extraction vessel, percent recovery is plotted as a function of the molar ratio of CO₂ passed through the extractor to organic solute loaded in the extractor. Phenol, benzoic acid, and benzamide, which are solids at room temperature, required the largest amounts of CO₂ for 95% solute recovery. Although the amounts of all solutes loaded into the extractor are well below the solubility limit, benzene and chlorobenzene, the two organics that exhibit phase immiscibility with [bmim][PF₆], required the least amount of CO₂ for recovery. Solute recovery

**Figure 2.** Extraction of aromatic solutes from [bmim][PF₆] with SCCO₂ at 40 °C and 138 bar. Solute dipole moments (Debye) shown in figure.**Figure 3.** Extraction of aliphatic solutes from [bmim][PF₆] with SCCO₂ at 40 °C and 138 bar. Solute dipole moments (Debye) shown in figure.

of hexane-based organics is shown in Figure 3. Hexanamide, a solid with the largest dipole moment of all the solutes tested, required twice the amount of CO₂ for solute recovery compared to the other hexane-based organics.

Discussion

Solubility Studies. We anticipate that the compounds that are most similar to [bmim][PF₆] will have the highest solubilities. [bmim][PF₆] is an interesting solvent in that its chemical structure consists of moieties that are very different in nature. As with all ionic liquids, [bmim][PF₆] is made up of cations and anions, but these ions are not solvated like ions from a salt dissolved in an aqueous solution. The cation is an aromatic ring, but the substituent on this ring is a simple aliphatic chain. Armstrong and co-workers have recently measured the retention times of a wide variety of solutes, including some of those investigated here, on a column coated with [bmim][PF₆].⁸ They found that [bmim][PF₆] has a dual nature. Nonpolar species are separated in much the same fashion as they are with nonpolar stationary phases, but highly polar molecules and proton-donor molecules are much more strongly retained than on a nonpolar column. In addition, recent studies with solvatochromic probes¹⁰ suggest that the overall solvent strength of [bmim][PF₆] is greater than that of an aprotic polar solvent, such as acetonitrile, but is less than that of water. This would place [bmim][PF₆] in the region of methanol and ethanol.

The solubility measurements clearly indicate that aromatic compounds are more soluble in [bmim][PF₆] than nonaromatic compounds of equivalent molecular weight and polarity. For example, the halogens, ethers, and ketones from the benzene and hexane families have comparable dipole moments, but the solubilities of the benzene-based compounds are several times greater than those of their hexane-based counterparts. In addition, benzene and chlorobenzene are the only aromatic liquids to exhibit immiscibility with [bmim][PF₆]. In contrast hexane, the smallest aliphatic, and 2-hexanone are the only miscible organics from the hexane family. Atwood and co-workers have shown that the high solubility of aromatic compounds in some molten salts can be attributed to liquid clathrate formation;¹¹ further work will have to be done to determine whether this phenomenon plays a role with these salts. The data also indicate that compounds with larger dipole moments, excluding the solid compounds, are generally completely miscible or very soluble in [bmim][PF₆]. Examples include acetophenone, benzaldehyde, 2-hexanone, and 1,4-butanediol. It should be noted that, for the solutes whose retention times on a [bmim][PF₆]-coated chromatography column were measured by Armstrong and co-workers,⁸ the retention factors do not correlate with the solubility measurements. This is not surprising as retention factors are measured essentially at infinite dilution and, therefore, reflect only solute/solvent interactions. By contrast, equilibrium solubilities reflect both solute/solvent and solute/solute interactions.

The solubilities of the solids in the IL are lower than those of the organic liquids, as expected, with phenol being the lone exception. For solid/liquid equilibrium, the requirement of equal fugacity in the two phases yields eq 1. If the liquid solution is an ideal solution, then the activity coefficient, γ , should be unity. Otherwise, any liquid-phase nonideality, whether the liquid is an organic mixture or an aqueous electrolyte solution, is described by the activity coefficient. Thus, the solubilities of solids in [bmim][PF₆] can be used to determine their activity coefficients in the IL-rich liquid phase. The only assumptions made in eq 1 are that the solubility of the liquid in the solid is negligible, that the normal

Table 2. Activity Coefficients of Solid Solutes in [bmim][PF₆] Calculated from Solubility Measurements at 22 °C

solute	T_m (K)	ΔH_{fus}^{12} (kJ/mol)	C_p (solid) ¹² (J mol ⁻¹ K ⁻¹)	C_p (liquid) ¹² (J mol ⁻¹ K ⁻¹)	γ
benzamide	403	23.760	153.8	274.2	4.08
phenol	314	11.514	127.2	199.8	1.11
benzoic acid	396	16.230	147.0	259	5.04

melting point temperature is a reasonable estimate of the triple-point temperature, and that the normal heat of fusion is a reasonable estimate for the enthalpy of fusion at the triple point.

$$\gamma = \exp \left[\frac{H_{fus} - \Delta C_p T_m}{RT_m} \left(\frac{T - T_m}{T} \right) - \frac{\Delta C_p}{R} \ln \left(\frac{T_m}{T} \right) - \ln x \right] \quad (1)$$

H_{fus} is the heat of fusion, ΔC_p is the difference of heat capacities between the solid and liquid phase of the solute, x is the mole fraction solubility of the solid in the solvent, T_m is the melting point of the solid, and γ is the activity coefficient of the solid in the liquid phase. The solid pure component properties were found in the National Institute of Standards and Technology database.¹² We were not able to find data for hexanamide. These parameters and the resulting activity coefficients, calculated from our experimental solubilities, are listed in Table 2 for three of the solids. The values of the activity coefficients suggest that the organic/IL mixtures are only slightly (phenol) or moderately (benzamide and benzoic acid) nonideal. Thus, it might be possible to model the phase behavior of organic/IL mixtures with conventional excess Gibbs free energy models. An alternative approach would be to start with the Debye-Huckel model, as the ILs are ionic. With these limited data, we have not yet attempted any modeling of the nonidealities in IL/organic mixtures.

Extraction Studies. As shown above, numerous types of organic compounds, polar and nonpolar, aromatic and aliphatic, volatile and nonvolatile, with a variety of chemical substituents, can all be extracted from [bmim][PF₆] with SCCO₂. This experimental work demonstrates and verifies the generality of the concept of utilizing SCCO₂ for product recovery from an IL, as previously proposed.⁵

The extraction cell used in these experiments is given 40 min to equilibrate before the solute-saturated CO₂ is passed through the restrictor for sample collection. From this fact, one might anticipate that the extracts are in thermodynamic equilibrium with the IL solutions. Although this is certainly true in some cases, it is clear that mass transfer limitations do play a role for some of the samples, especially toward the end of the extractions when only a small amount of solute remains in the IL. Nonetheless, the extraction curves follow reasonable trends in the expected thermodynamic equilibrium distribution coefficients, as will be shown below. Thus, we will concentrate on analyzing the results in terms of thermodynamics, with the full knowledge that this is just one of the important factors in supercritical fluid extraction.

An important thermodynamic property is the distribution coefficient, K , the ratio of the solute mole fractions in the supercritical and IL phases, respectively.

$$K = \frac{y}{x} \quad (2)$$

These experiments represent a liquid mixture in equilibrium with a supercritical fluid mixture. If the liquid phase is modeled with an equation of state the distribution coefficient is given by

$$K = \frac{\varphi_{\text{liq}}}{\varphi_{\text{SCF}}} \quad (3)$$

Conversely, if the liquid phase is modeled with an activity coefficient, this distribution coefficient is given by

$$K = \frac{\gamma P_{\text{sat}} \exp \int_{P_2}^P \frac{v_2^S}{RT} dP}{\varphi P} \quad (4)$$

In either case, the distribution coefficient is determined by the nonideality of the solute in the supercritical fluid and liquid phases (as given by ϕ and/or γ). Because [bmim][PF₆] does not dissolve appreciably in the CO₂, the supercritical phase is essentially organic solute and CO₂. The fugacity coefficient of the solute in the supercritical fluid phase, then, is quite familiar and can be estimated with a simple equation of state like Peng–Robinson.¹³ From much experience with measurements of solubilities of solutes in SCCO₂, we know that these fugacity coefficients can be very small numbers, which, in turn, result in relatively large solubilities in SCFs. Because we are able to understand these fugacity coefficients, the underlying question rests on the nonideality in the liquid phase. The liquid phase is a mixture of solute and IL. However, previous work indicates that a large amount of CO₂ will be dissolved in the IL-rich phase.⁵ In fact, at 138 bar, the solubility of CO₂ in the [bmim][PF₆] phase might be as high as 0.85 mole fraction CO₂. With this knowledge, combined with the solute–IL solubility measurements, we can anticipate the trends of the distribution coefficients. High volatility and low polarity will favor the solubility of a solute in CO₂, as seen by a larger y value. In contrast, high polarity and aromaticity will favor solute solubility in the IL-rich liquid phase, as indicated by a larger x value.

The compounds that required the greatest amounts of CO₂ to achieve 95% recovery were the four solid solutes (Figure 4). The solid solutes have a wide range of polarities, yet their solubilities in the CO₂ phase are quite small.^{14,15} Thus, the dominant factor in determining the distribution coefficient is the small y value due to the low volatility of the solid solutes. Although many solids are soluble in the SCCO₂ phase, their solubilities are, in general, significantly less than those of liquids. We are able to examine the effect of polarity through the behavior of the liquid organic solutes. Solute with high polarities should have a large affinity for the IL phase and a low affinity for the CO₂, giving small K values. Conversely, nonpolar solutes should have a greater affinity for CO₂ and, except for the smallest compounds, should have a relatively low affinity for the IL, resulting in large K values.

For the liquid solutes, a correlation exists between the amount of CO₂ necessary for 95% extraction and the dipole moment of the solute. Figure 4 illustrates the number of moles of CO₂ per mole of organic solute

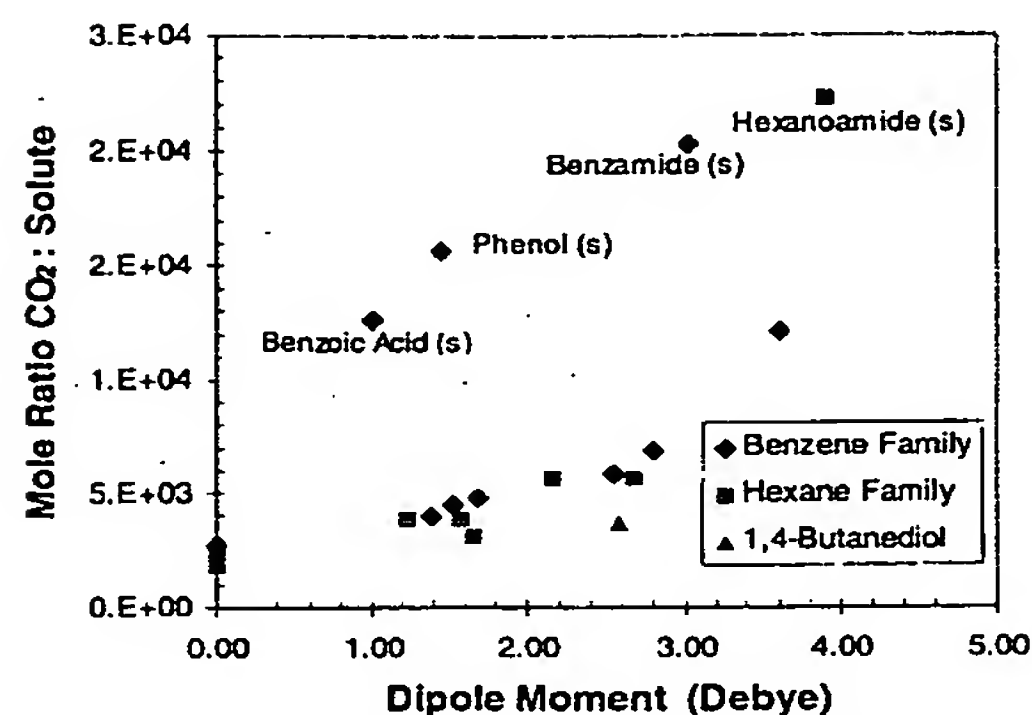


Figure 4. Effect of solute dipole moment on ease of extraction of solutes from [bmim][PF₆] with SCCO₂ at 40 °C and 138 bar.

Table 3. CO₂–Liquid Organic Solute Binary Phase Behavior

binary system	pressure ^a (bar)	mole ratio CO ₂ :solute for 95% recovery
CO ₂ –hexane ¹⁶	54.1	2.34E+03
CO ₂ –benzene ¹⁶	59.6	2.75E+03
CO ₂ –anisole ¹⁷	60.8	4.00E+03
CO ₂ –cyclohexane ¹⁸	64.8	1.84E+03
CO ₂ –chlorobenzene ¹⁹	66.7	4.77E+03
CO ₂ –methyl benzoate ²⁰	71.0	5.87E+03
CO ₂ –acetophenone ²¹	75.4	2.03E+04
CO ₂ –benzaldehyde ¹⁹	77.8	6.85E+03

^a Pressure required to dissolve 70 mol % CO₂ in the liquid phase at 40 °C.

needed to extract 95% of the solute from [bmim][PF₆] as a function of the solute dipole moment. The three organics with a dipole moments of zero, namely, benzene, hexane, and cyclohexane, are easily extracted, requiring approximately half the number of moles of CO₂ required for solutes with a higher polarity. Not only do solutes from both families have equivalent extents of solute recoverability, but the amounts of CO₂ necessary to achieve such extractions rates are comparable based on the substituent group of the solute, as indicated by the overlapping trends of Figure 4. For example, the ethers anisole and butyl ethyl ether, with dipole moments of 1.38 and 1.22 D, have CO₂-to-solute molar ratios of 4.00E+03 and 3.96E+03, respectively.

Another source of insight on the ease of extraction of these compounds can be obtained from the phase behavior of the organic solute–CO₂ binary systems. Of the 16 liquid solutes studied, there are literature measurements of phase behavior with CO₂ for 8 of them. Because all of these binary pairs are completely miscible with CO₂ at 40 °C and 138 bar, their affinities for CO₂ cannot be expressed in terms of solubility in CO₂ (Table 3). Nonetheless, a measure of affinity of these compounds for CO₂ can be determined from the liquid-phase data at lower pressures. For example, compounds in which CO₂ readily dissolves at low pressures have a greater attraction for CO₂. Thus, we have arbitrarily chosen the pressure required to dissolve 70 mol % CO₂ in the liquid phase at 40 °C as a measure of the CO₂-philicity of the solutes. These pressures are plotted as a function of the ratio of the number of moles of CO₂ per mole of solute needed to achieve 95% recovery in the extraction studies. The results are shown in Figure 5. Clearly, the compounds that have a greater affinity for CO₂ are more easily extracted from the IL mixture.

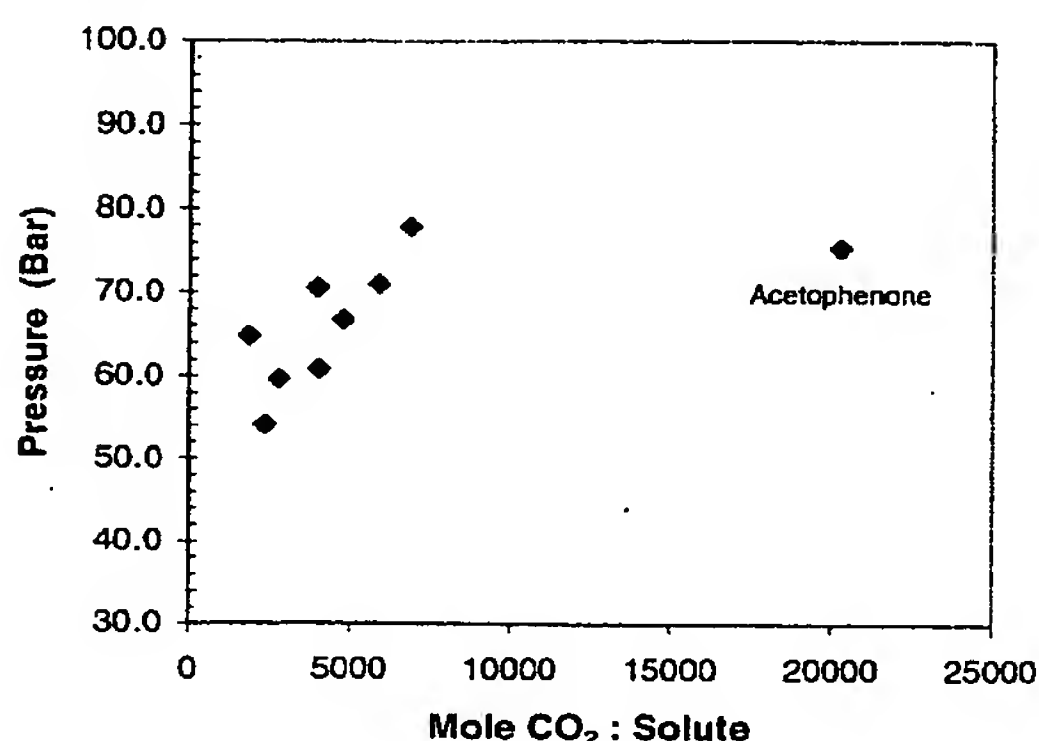


Figure 5. Effect of solute CO_2 -philic nature on ease of extraction of solutes from [bmim][PF₆] with SCCO₂ at 40 °C and 138 bar.

To further explore the applicability of SCCO₂ for the separation of a solute from an ionic liquid, a high-boiling-point organic liquid was extracted from [bmim][PF₆]. 1,4-Butanediol, with a boiling temperature of 230 °C, followed the same solubility and extractability trends as the other liquid solutes. Solute recovery from [bmim][PF₆] was 95%. Using SCCO₂ to recover a high-boiling-point solute, an instance in which distillation would not be a prudent option, further emphasizes the applicability of supercritical fluid extraction for the recovery of compounds from ionic liquids.

Conclusions

The development of ionic liquids in recent years has opened numerous avenues in the areas of reaction chemistry and process development while maintaining an environmental sustainability emphasis. This work has shown that CO_2 can completely extract a wide array of organic solutes from an ionic liquid. By employing CO_2 for product recovery, we are able not only to quantitatively extract all of an organic solute from an ionic liquid but also to eliminate the problem of IL contamination in the recovered product. Using hexane and benzene as roots to which several types of substituent groups were added, a correlation relating dipole moment to the amount of CO_2 necessary for solute recovery has been established. Intermolecular interactions between the organics and [bmim][PF₆], although influential in the solubility of the solute in the IL, do not limit the degree to which a solute can be separated from the IL. Overall, ionic liquids and supercritical CO_2 offer not only a new avenue for reactions and separations but have the additional asset of environmental sustainability.

Acknowledgment

Financial support from the Environmental Protection Agency (Grant R826734-01-0), the National Science Foundation (Grant EE697-00537-CRCD), and a Clare Booth Luce Fellowship are gratefully acknowledged.

Literature Cited

- (1) Seddon, K. R. Room-Temperature Ionic Liquids: Neoteric Solvents for Clean Catalysis. *Kinet. Catal.* **1996**, *37*, 693–697.
- (2) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071.
- (3) Huddleston, J. G.; Willauer, H. D.; Swatoski, R. P.; Visser, A. E.; Rogers, R. D. Room-Temperature Ionic Liquids as Novel

Media for 'Clean' Liquid-Liquid Extraction. *Chem. Commun.* **1998**, *16*, 1765.

(4) Earle, M. J.; McCormac, P. B.; Seddon, K. R. Diels-Alder Reactions in Ionic Liquids. *Green Chem.* **1999**, *1*, 23.

(5) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. Green Processing Using Ionic Liquids and CO_2 . *Nature* **1999**, *399*, 28.

(6) Blanchard, L. A.; Gu, Z.; Brennecke, J. F. High-Pressure Phase Behavior of Ionic Liquid/ CO_2 Systems. Submitted for publication.

(7) Dullius, J. E. L.; Suarez, P. A.; Einloft, S.; de Souza, R. F.; Dupont, J. Selective Catalytic Hydrodimerization of 1,3-Butadiene by Palladium Compounds Dissolved in Ionic Liquids. *Organometallics* **1998**, *17*, 815.

(8) Armstrong, D. W.; He, L.; Liu, Y.-S. Examination of Ionic Liquids and Their Interaction with Molecules, When Used as Stationary Phases in Gas Chromatography. *Anal. Chem.* **1999**, *71*, 3873.

(9) McClellan, A. *Tables of Experimental Dipole Moments*; Rahara Enterprises: El Cerrito, CA, 1974; Vol. 2.

(10) Aki, S. N.; Brennecke, J. F.; Samanta, A. How Polar are Room-Temperature Ionic Liquids? Submitted for publication.

(11) Atwood, J. L. Liquid Clathrates, in *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1.

(12) Domalski, E. S.; Hearing, E. D. *Condensed Phase Heat Capacity Data in NIST Chemistry WebBook*; NIST Standard Reference Database Number 69; National Institute of Standards and Technology: Gaithersburg, MD, 2000, (<http://webbook.nist.gov>).

(13) Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.

(14) Schmitt, W. J.; Reid, R. Solubility of Monofunctional Organic Solids in Chemically Diverse Supercritical Fluids. *J. Chem. Eng. Data*, **1986**, *31*, 204.

(15) Van Leer, R. A.; Paulaitis, M. E. Solubilities of Phenol and Chlorinated Phenols in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1980**, *25*, 257.

(16) Ohgaki, K.; Katayama, T. Isothermal Vapor-Liquid Equilibrium Data for Binary Systems Containing Ethane at High Pressures. *J. Chem. Eng. Data* **1976**, *21*, 55.

(17) Park, S.; Kim, C.; Choi, C. High-Pressure Binary Vapor-Liquid Equilibrium Measurements of Carbon Dioxide and Aromatic Hydrocarbons. *J. Chem. Eng. Data* **1991**, *36*, 80.

(18) Al-Sahhaf, T. A.; Al-Ameeri, R. S.; Hamam, S. E. Bubble Point Measurements for the Ternary System: CO_2 , Cyclohexane, and Naphthalene. *Fluid Phase Equilib.* **1989**, *53*, 31.

(19) Walther, D.; Maurer, G. High-Pressure Vapor-Liquid Equilibria in Binary Mixtures of Carbon Dioxide and Benzaldehyde, Bromobenzene, Chlorobenzene, 1,2-Dichlorobenzene and 2-Chloro-1-methylbenzene at Temperatures Between 313 and 393 K and Pressures up to 22 MPa. *Berichte der Bunsen-Ges. Phys. Chem.* **1992**, *96*, 981.

(20) Bamberger, A.; Maurer, G. High-Pressure Vapor-Liquid Equilibria in Binary Mixtures of Carbon Dioxide and Aromatic Hydrocarbons: Experimental Data and Correlation for CO_2 + Acetophenone, CO_2 + 1-Chloronaphthalene, CO_2 + Methyl Benzoate and CO_2 + *n*-Propylbenzene. *J. Supercrit. Fluids* **1994**, *7*, 115.

(21) Weng, W. L.; Lee, M. J. Vapor-Liquid Equilibrium for Binary Systems Containing a Heavy Liquid and a Dense Fluid. *Ind. Eng. Chem. Res.* **1992**, *31*, 2769.

Received for review July 31, 2000

Revised manuscript received September 29, 2000

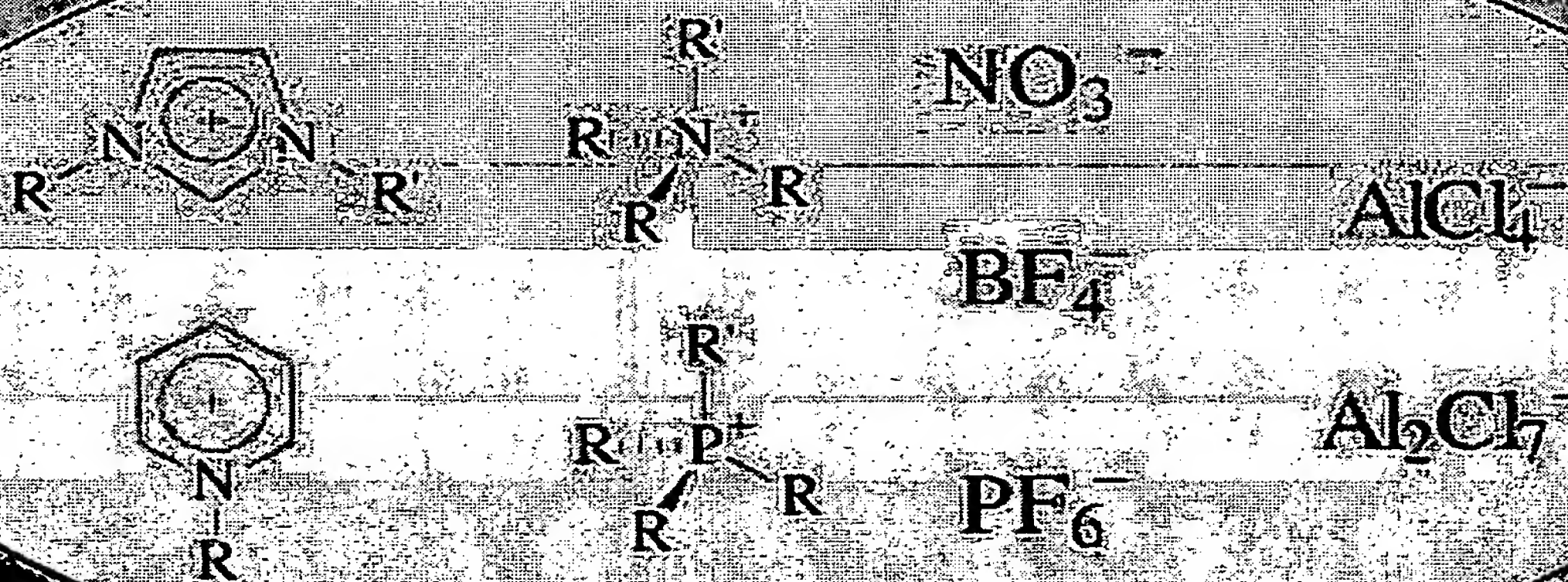
Accepted October 3, 2000

IE000710D

Edukt/Produktphase



[Katalysator]⁺ [Anion]⁻
ionische Flüssigkeit



Ionische Flüssigkeiten – neue „Lösungen“ für die Übergangsmetallkatalyse

Peter Wasserscheid* und Wilhelm Keim

Ionische Flüssigkeiten sind bei niedrigen Temperaturen ($<100^{\circ}\text{C}$) schmelzende Salze, die eine neuartige Klasse von Lösungsmitteln mit nichtmolekularem, ionischem Charakter darstellen. Auch wenn einige bereits seit 1914 bekannt sind, wurden ionische Flüssigkeiten erst in den letzten zehn Jahren intensiv als Lösungsmittel für die Übergangsmetallkatalyse untersucht. Die seither erschienenen Veröffentlichungen belegen, dass der Ersatz organischer Lösungsmittel durch eine

ionische Flüssigkeit zu bemerkenswerten Verbesserungen bekannter Verfahren führen kann: Mit vielen organischen Produktgemischen bilden ionische Flüssigkeiten zwei Phasen. Daraus ergibt sich die Möglichkeit einer mehrphasigen Reaktionsführung zur problemlosen Abtrennung homogener Katalysatoren. Außerdem haben ionische Flüssigkeiten praktisch keinen Dampfdruck, was eine destillative Produktabtrennung stark vereinfacht. Darüber hinaus gibt es Hinweise, dass

der Übergang von einem „üblichen“ organischen Lösungsmittel zu einer ionischen Flüssigkeit zu einer neuartigen und ungewöhnlichen chemischen Reaktivität führen kann. Dies öffnet ein weites Feld für zukünftige Untersuchungen dieser neuartigen Lösungsmittelklasse in katalytischen Anwendungen.

Stichwörter: Homogene Katalyse • Ionische Flüssigkeiten • Lösungsmittelleffekte • Zweiphasenkatalyse

1. Einleitung

Unter einer ionischen Flüssigkeit versteht man allgemein eine Flüssigkeit, die ausschließlich aus Ionen besteht. Allerdings enthält der Begriff in seiner spezielleren Definition zusätzlich eine Abgrenzung vom klassischen Begriff der Salzschnmelze:^[1] Während man bei Salzschnmelzen gewöhnlich an hochschmelzende, hochviskose und sehr korrosive Medien denkt, sind ionische Flüssigkeiten bereits bei niedrigen Temperaturen ($<100^{\circ}\text{C}$) flüssig und relativ niedrigviskos. Die zunächst etwas willkürlich anmutende Grenzziehung zwischen Salzschnmelzen und ionischen Flüssigkeiten bei einer Schmelztemperatur von 100°C lässt sich durch die sprunghafte Verbesserung der Anwendungsbreite flüssiger Salze unterhalb dieser Temperatur rechtfertigen: Auch wenn einige Beispiele bekannt geworden sind, in denen Hochtemperatur-Salzschnmelzen erfolgreich als Reaktionsmedien in präparativen Anwendungen eingesetzt wurden,^[2] erlaubt doch erst ein Flüssigkeitsbereich bis unter 100°C die vielfältige Substitution konventioneller, organischer Lösungsmittel.

Die Entwicklung ionischer Flüssigkeiten reicht bis in das Jahr 1914 zurück. Die ersten Arbeiten beschäftigten sich mit der Herstellung von Ethylammoniumnitrat.^[3] Das Salz liegt bei Raumtemperatur flüssig vor, enthält aber eine geringe Menge an Wasser (200–600 ppm).^[4]

Die ersten ionischen Flüssigkeiten mit Chloroaluminat-Ionen wurden 1948 von Hurley und Wier am Rice Institute in Texas als Badflüssigkeit zum Elektroplatinieren von Aluminium entwickelt.^[5] Diese Systeme wurden jedoch erst Ende der siebziger Jahre von den Gruppen um Osteryoung und Wilkes wieder aufgegriffen. Dabei gelang es erstmals, bei Raumtemperatur flüssige Chloroaluminat-Schnmelzen zu entwickeln.^[6] Die Forschungs- und Entwicklungsarbeiten in dieser Zeit konzentrierten sich vor allem auf Anwendungen im Bereich der Elektrochemie.

Bereits 1967 erschien ferner eine Arbeit von Swain et al., in der Tetra-*n*-hexylammoniumbenzoat als Lösungsmittel für kinetische und elektrochemische Untersuchungen beschrieben wurde.^[7] Auch wenn das bei Raumtemperatur flüssige Salz als Hemihydrat vorliegt, ist diese Veröffentlichung von wegweisender Bedeutung, da sie bereits eine quantitative Bestimmung der Ionisierungskraft des untersuchten ionischen Mediums enthält.

Anfang der achtziger Jahre begannen die Gruppen um Seddon und Hussey, Chloroaluminat-Schnmelzen als nichtwässrige, polare Lösungsmittel zur Untersuchung von Übergangsmetallkomplexen zu nutzen. Meist wurden zunächst elektrochemische Aspekte der entsprechenden Übergangs-

[*] Dr. P. Wasserscheid, Prof. W. Keim
Institut für Technische Chemie und Makromolekulare Chemie der RWTH Aachen
Worringer Weg 1, 52074 Aachen (Deutschland)
Fax: (+49) 241-8888177
E-mail: Wasserscheidp@itc.rwth-aachen.de

metallchlorokomplexe untersucht,^[8] spektroskopische und komplexchemische Arbeiten folgten.^[9] Vor allem die Arbeiten von Seddon haben geholfen, ionische Flüssigkeiten einer breiten Öffentlichkeit vertraut zu machen.

Die ersten Publikationen, in denen ionische Flüssigkeiten als neue Reaktionsmedien und Katalysatoren für die organische Synthese beschrieben wurden, erschienen Ende der achtziger Jahre: Acide ionische Flüssigkeiten mit Chloroaluminat-Ionen erwiesen sich als effektive Friedel-Crafts-Katalysatoren,^[10] und Phosphoniumhalogenid-Schmelzen konnten erfolgreich als Reaktionsmedien in nucleophilen aromatischen Substitutionen eingesetzt werden.^[11]

Die Verwendung ionischer Flüssigkeiten als Lösungsmittel für homogene Übergangsmetallkatalysatoren wurde erstmals 1990 von Chauvin et al. sowie Wilkes et al. beschrieben. Die Gruppe um Chauvin löste Nickelverbindungen in schwach aciden Chloroaluminat-Schmelzen und untersuchte die katalytischen Eigenschaften der resultierenden ionischen Katalysatorlösungen in der Dimerisierung von Propen.^[12] Wilkes et al. führten ebenfalls in schwach aciden Chloroaluminat-Schmelzen Versuche zur Ethenpolymerisation mit Ziegler-Natta-Katalysatoren durch.^[13]

Eine beträchtliche Erweiterung erfuhr das Konzept der ionischen Flüssigkeiten wiederum durch die Gruppe um Wilkes, die 1992 die Synthese von deutlich hydrolysestabilen ionischen Flüssigkeiten, z. B. solchen mit Tetrafluoroborat-Ionen, beschrieb.^[14] Im Unterschied zu Chloroaluminat-Schmelzen bieten diese Systeme eine hohe Toleranz gegenüber Molekülen mit funktionellen Gruppen, was zahlreiche neue Einsatzbereiche im Bereich der Übergangsmetallkatalyse erschließt. So konnten von Chauvin ionische Flüssigkeiten mit Tetrafluoroborat-Ionen erfolgreich in der rho-

diumkatalysierten Hydroformylierung von Olefinen eingesetzt werden.^[15]

Aufbauend auf Wilkes' Arbeiten setzte sich die Erkenntnis durch, dass ionische Flüssigkeiten keineswegs auf Chloroaluminat-Schmelzen beschränkt sind, sondern im Gegenteil eine ganze Reihe von Kation/Anion-Kombinationen niedrig schmelzende Salze bilden können.

Jüngste Publikationen beschäftigen sich mit der Synthese neuer ionischer Flüssigkeiten,^[16] mit der systematischen Untersuchung ihrer physikalischen und chemischen Eigenschaften^[17] sowie mit weiteren Anwendungen als Lösungsmittel und als Katalysatoren.^[18]

In zwei hervorragenden Übersichtsartikeln von Welton^[19] sowie Seddon und Holbrey^[20] ist vor allem die Verwendung von Chloroaluminat-Schmelzen in präparativen und katalytischen Reaktionen umfassend beschrieben. Auch elektrochemische^[21] und komplexchemische Untersuchungen^[22] in ionischen Flüssigkeiten waren bereits Gegenstand umfangreicher Übersichten.

Ziel unseres Beitrags ist es, Synthese, Eigenschaften und Potential ionischer Flüssigkeiten im Hinblick auf Anwendungen im Bereich der Übergangsmetallkatalyse vorzustellen. Dabei wollen wir insbesondere dem homogenkatalytisch arbeitenden Chemiker Kriterien an die Hand geben, um aus der großen Zahl ionischer Flüssigkeiten (einige Autoren sprechen von bis zu 10¹⁸ möglichen Kation/Anion-Kombinationen^[20]) eine Vorauswahl treffen zu können. Im Anschluss soll eine Auswahl von Beispielen belegen, dass die Übergangsmetallkatalyse in ionischen Flüssigkeiten in vielen Fällen eine erfolgreiche Alternativ-„Lösung“ sein kann. Besondere Aufmerksamkeit kommt hierbei jüngsten Arbeiten zur Übergangsmetallkatalyse in „Nicht-Chloroaluminat“-Systemen zu.

Peter Wasserscheid, geboren 1970 in Würzburg, studierte an der RWTH Aachen Chemie und promovierte 1998 im Arbeitskreis von W. Keim mit einer Arbeit über die Ni-katalysierte C-C-Verknüpfung in ionischen Flüssigkeiten. Zurzeit habilitiert er sich am Institut für Technische Chemie und Makromolekulare Chemie der RWTH Aachen und beschäftigt sich dort mit weiteren Anwendungen ionischer Flüssigkeiten in synthetischen und katalytischen Reaktionen. Schon früh fand seine wissenschaftliche Betätigung durch einen 1. Preis im Bundeswettbewerb „Jugend forscht“ Anerkennung. Für herausragende Leistungen in Studium und Diplomarbeit erhielt er den DECHEMA-Studentenpreis und den Friedrich-Wilhelm-Preis der RWTH Aachen.



P. Wasserscheid



W. Keim

Wilhelm Keim, geboren 1934 in Oberhausen, studierte Chemie und promovierte 1963 bei G. Wilke am Max-Planck-Institut für Kohlenforschung. Nach einem Jahr als Postdoc bei T. Kalz an der Columbia University, New York, trat er in die Shell Development Company in Emeryville, CA, ein. Bis 1972 avancierte er dort zum Leiter der Grundlagenforschung. 1973 nahm er einen Ruf als Professor und Institutsdirektor des Instituts für Technische Chemie und Petrolchemie der RWTH Aachen an. Seine Forschungstätigkeit umfasst Arbeiten zur homogenen und heterogenen Katalyse, zur Carbonylierung und Funktionalisierung von Olefinen sowie zur selektiven C-C-Verknüpfung. In diesem Zusammenhang bearbeitete er intensiv Fragestellungen zur Heterogenisierung homogener Katalysatoren und zur Zweiphasenkatalyse. Er ist Autor von rund 200 Veröffentlichungen und 40 Patenten. Sein wissenschaftliches Werk wurde in jüngster Zeit mit der Alwin-Mittasch- sowie der Karl-Engler-Medaille gewürdigt.

2. Synthese der ionischen Flüssigkeiten

Bei der Synthese ionischer Flüssigkeiten wird zunächst durch Quaternisierung, etwa eines Amins oder Phosphans, das Kation aufgebaut.^[6c, 23] Die wichtigsten, beschriebenen Kationtypen werden in Schema 1 vorgestellt.



Imidazolium-Ion Pyridinium-Ion Ammonium-Ion Phosphonium-Ion
Schema 1. Wichtige Arten von Kationen in ionischen Flüssigkeiten.

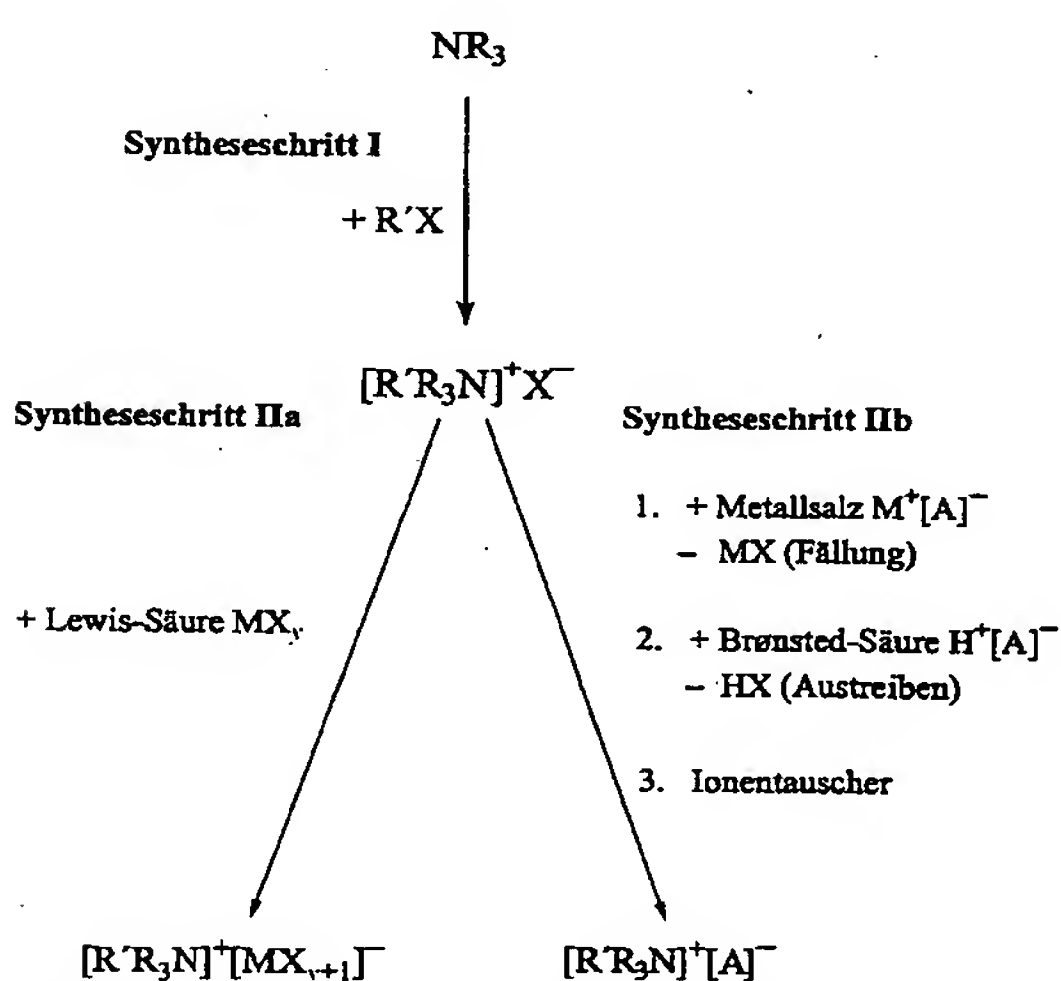
Je nach verwendetem Alkylierungsreagens werden bei der Quaternisierung Salze mit unterschiedlichen Anionen erhalten. Interessanterweise ergeben sich für eine Reihe der so zugänglichen Kation/Anion-Kombinationen bereits Schmelzpunkte, die unter 100 °C liegen (Tabelle 1).

Tabelle 1. Beispiele für ionische Flüssigkeiten, die durch direkte Quaternisierung gebildet werden können.

ionische Flüssigkeit	Alkylierungsreagens	Schmp. [°C]	Lit.
[EMIM]CF ₃ SO ₃ ^[a]	Methyltriflat	–9	[16a]
[BMIM]CF ₃ SO ₃ ^[b]	Methyltriflat	16	[16a]
[Ph ₃ POc]OTs ^[c]	OcOTs	70–71	[24]
[Bu ₃ NMe]OTs	MeOTs	62	[25]
[BMIM]Cl	Chlorbutan	65–69	[6c]

[a] EMIM = 1-Ethyl-3-methylimidazolium-Ion; CF₃SO₃ = Triflat-Anion.
[b] BMIM = 1-*n*-Butyl-3-methylimidazolium-Ion. [c] Oc = Octyl; Ts = H₃CC₆H₄SO₂ (Tosyl).

In Fällen, in denen es nicht möglich ist, das gewünschte Anion bereits bei der Quaternisierung zu bilden, erfolgt dies in einem weiteren Syntheseschritt (Syntheseschritt IIa oder IIb in Schema 2). Ausgehend beispielsweise von einem



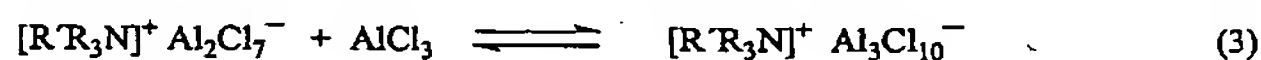
Schema 2. Synthesewege zur Herstellung ionischer Flüssigkeiten am Beispiel eines Ammoniumsalzes.

Ammoniumhalogenid [R'R₃N]⁺X[–] sind zwei Wege zur Variation des Anions möglich. Zum einen kann das Halogenid [R'R₃N]⁺X[–] mit einer Lewis-Säure MX_y umgesetzt werden. Dabei wird eine ionische Flüssigkeit vom Typ [R'R₃N]⁺[MX_{y+1}][–] gebildet (Syntheseschritt IIa in Schema 2). Alternativ dazu ist ein Austausch des Halogenidions X[–] gegen das gewünschte Anion möglich. Dies kann durch Zugabe eines Metallsalzes M⁺[A][–] (unter Ausfällung von M⁺X[–]), über einen Ionenaustauscher oder durch Verdrängung des Halogenidions durch eine starke Säure H⁺[A][–] (unter Freisetzung von H⁺X[–]) geschehen (Syntheseschritt IIb in Schema 2).

Im ersten Fall liegen oft mehrere Anionen in einem Gleichgewicht vor, das vom eingesetzten Verhältnis der beiden Komponenten [R'R₃N]⁺X[–] und MX_y abhängt [Gl. (1)].



Bei Verwendung der Lewis-Säure MX_y im Überschuss können sich zusätzliche Anionspezies bilden, wenn es zu einer weiteren Säure-Base-Reaktion mit dem bereits gebildeten Anion kommt. Ein solches Verhalten zeigen beispielsweise Chloroaluminat-Schmelzen [Gl. (2), (3)].^[26] Die Bildung der



verschiedenen Anionen erfolgt hier in Abhängigkeit vom eingesetzten Chlorid/AlCl₃-Verhältnis. Man erkennt aus Abbildung 1, dass bei der Zugabe von Aluminiumtrichlorid zum

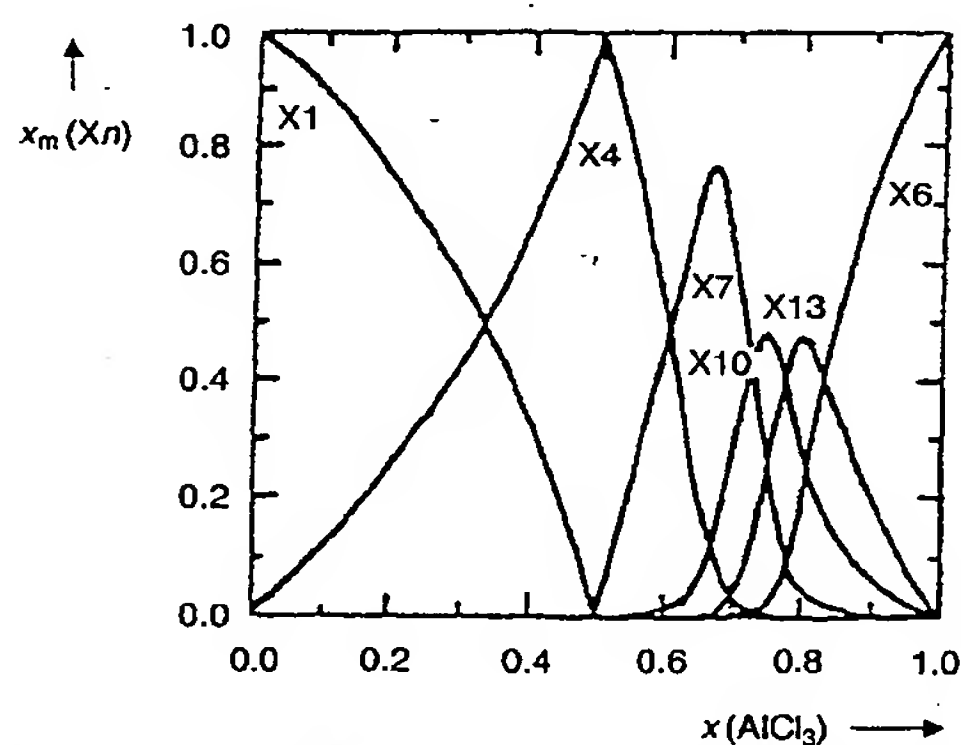


Abbildung 1. Molarer Anteil x_m verschiedener Anionenspezies X_n in Chloroaluminat-Schmelzen ($X_1 = \text{Cl}^-$; $X_4 = \text{AlCl}_4^-$; $X_7 = \text{Al}_2\text{Cl}_7^-$; $X_{10} = \text{Al}_3\text{Cl}_{10}^-$; $X_{13} = \text{Al}_4\text{Cl}_{13}^-$; $X_6 = \text{Al}_2\text{Cl}_6$).

Chlorid zunächst das Anion AlCl_4^- gebildet wird. Bei einem Aluminiumtrichloridanteil von genau 0.5 liegt praktisch nur dieses Anion vor. In Systemen mit $x(\text{AlCl}_3) > 0.5$ bilden sich mehrkernige Chloroaluminat-Anionen, die untereinander, mit dem AlCl_4^- -Ion und bei sehr hohem AlCl_3 -Gehalt auch mit dimerem Aluminiumtrichlorid im Gleichgewicht stehen.^[26]

Chloroaluminat-Schmelzen sind zwar am gründlichsten untersucht, aber keineswegs die einzigen ionischen Flüssigkeiten, die durch Reaktion eines Halogenids mit einer Lewis-Säure hergestellt werden können. Weitere Beispiele werden in Tabelle 2 vorgestellt.

Tabelle 2. Beispiele für ionische Flüssigkeiten, die durch Reaktion eines Halogenids mit einer Lewis-Säure hergestellt werden können.

ionische Flüssigkeit ^[a]	nachgewiesene Anionen	Lit.
[Kation]Cl/AlCl ₃	Cl ⁻ , AlCl ₄ ⁻ , Al ₂ Cl ₇ ⁻ , Al ₃ Cl ₁₀ ⁻	[27]
[Kation]Cl/AlEtCl ₂	AlEtCl ₃ ⁻ , Al ₂ Et ₂ Cl ₅ ⁻	[28]
[Kation]Cl/BCl ₃	Cl ⁻ , BCl ₄ ⁻	[29]
[Kation]Cl/CuCl	CuCl ₂ ⁻ , Cu ₂ Cl ₃ ⁻ , Cu ₃ Cl ₄ ⁻	[30]
[Kation]Cl/SnCl ₂	SnCl ₃ ⁻ , Sn ₂ Cl ₅ ⁻	[31]

[a] Kation = Pyridinium- oder Imidazolium-Ion.

Im Fall der Variation des Anions durch Anionenaustausch (Syntheseschritt IIb in Schema 2) werden ionische Flüssigkeiten des Typs [Kation]⁺[A]⁻ gebildet, die bei vollständiger Austauschreaktion nur eine Anionspezies enthalten (Tabelle 3).

Tabelle 3. Beispiele für ionische Flüssigkeiten, die durch Anionenaustausch hergestellt werden können.

ionische Flüssigkeit ^[a]	Lit.
[Kation]BF ₄	[14, 32]
[Kation]PF ₆	[32, 33]
[Kation]SbF ₆	[30]
[Kation]NO ₃	[14]
[Kation]CH ₃ CO ₂	[14]
[Kation]HSO ₄	[16f]
[Kation]BEt ₃ Hex	[34]

[a] Kation = Pyridinium-, Imidazolium- oder Ammonium-Ion.

An dieser Stelle ist anzumerken, dass die Synthese hochreiner, binärer ionischer Flüssigkeiten besondere Anforderungen an das präparative Arbeiten stellt. Die Reinheit der Systeme ist für Anwendungen als Lösungsmittel sowie zur Bestimmung der physikalischen und chemischen Eigenschaften wesentlich. Während organische Lösungsmittel vor dem Gebrauch üblicherweise destillativ gereinigt werden, ist ein solches Verfahren auf Grund des nichtflüchtigen Charakters ionischer Flüssigkeiten zu deren Reinigung nicht möglich. Folglich muss bereits bei der Synthese binärer Systeme eine möglichst hohe Reinheit angestrebt werden. Beim Austausch eines Chlorid-Ions gegen das jeweils gewünschte Anion muss z. B. sichergestellt werden, dass keine Halogenidionen im System verbleiben. Auch Rückstände der zur Synthese verwendeten Säure können zu einer unerwünschten chemischen Reaktivität führen. Hohe Reinheiten bei der Synthese binärer ionischer Flüssigkeiten gewährleistet in der Regel der Anionenaustausch über einen Ionenaustauscher.

Natürlich können die beschriebenen Methoden auch genutzt werden, um bisher unbekannte Kombinationen von Kationen und Anionen herzustellen, die ebenfalls zu niedrig schmelzenden Salzen führen können. Außerdem besteht die Möglichkeit, durch Mischen mehrerer unterschiedlicher Salze zu ionischen Flüssigkeiten mit neuen Eigenschaften zu gelangen.^[35]

3. Charakteristische Eigenschaften ionischer Flüssigkeiten

Die physikalischen und chemischen Eigenschaften ionischer Flüssigkeiten lassen sich durch die geeignete Auswahl der verwendeten Kationen und Anionen in einem weiten Bereich gezielt variieren. Dabei besteht die Möglichkeit, durch stufenweise Abstimmung relevanter Lösungsmitelegenschaften das ionische Reaktionsmedium auf ein konkretes Anwendungsziel hin zu optimieren. In einigen Veröffentlichungen werden ionische Flüssigkeiten aus diesem Grund als „designer solvents“ bezeichnet.^[36]


Im folgenden Abschnitt wird versucht, die Beziehungen zwischen den Strukturmerkmalen einer ionischen Flüssigkeit und ihren wichtigsten physikalischen und chemischen Eigenschaften an einigen ausgewählten Beispielen darzustellen.

3.1. Schmelzpunkt

Zentrales Kriterium zur Beurteilung ionischer Flüssigkeiten ist definitionsgemäß ihr Schmelzpunkt. Von besonderer Bedeutung ist daher die Frage, welche Beziehung zwischen der Struktur und der chemischen Zusammensetzung einer ionischen Flüssigkeit und der Lage ihres Schmelzpunktes besteht.

Ein Vergleich der Schmelzpunkte unterschiedlicher Chloridsalze macht den Einfluss des Kations deutlich: Während für Alkalichloride hohe Schmelzpunkte charakteristisch sind, weisen Chloride mit geeigneten organischen Kationen Schmelztemperaturen unter 150 °C auf (Tabelle 4).^[6c, 37]

Tabelle 4. Schmelzpunkte unterschiedlicher Chloride.

Salz	Schmp. [°C]
NaCl	803
KCl	772
 Cl ⁻	R = R' = Me ([MMIM]Cl) ^[a] 125 R = Me, R' = Et ([EMIM]Cl) 87 R = Me, R' = nBu ([BMIM]Cl) 65

[a] MMIM = 1,3-Dimethylimidazolium-Ion.

In der Literatur werden folgende Merkmale für Kationen niedrig schmelzender Salze diskutiert: Niedrige Symmetrie,^[1] geringe intermolekulare Wechselwirkungen (etwa durch die Vermeidung von Wasserstoffbrückenbindungen)^[16a, 38] und eine gute Ladungsverteilung.^[39]

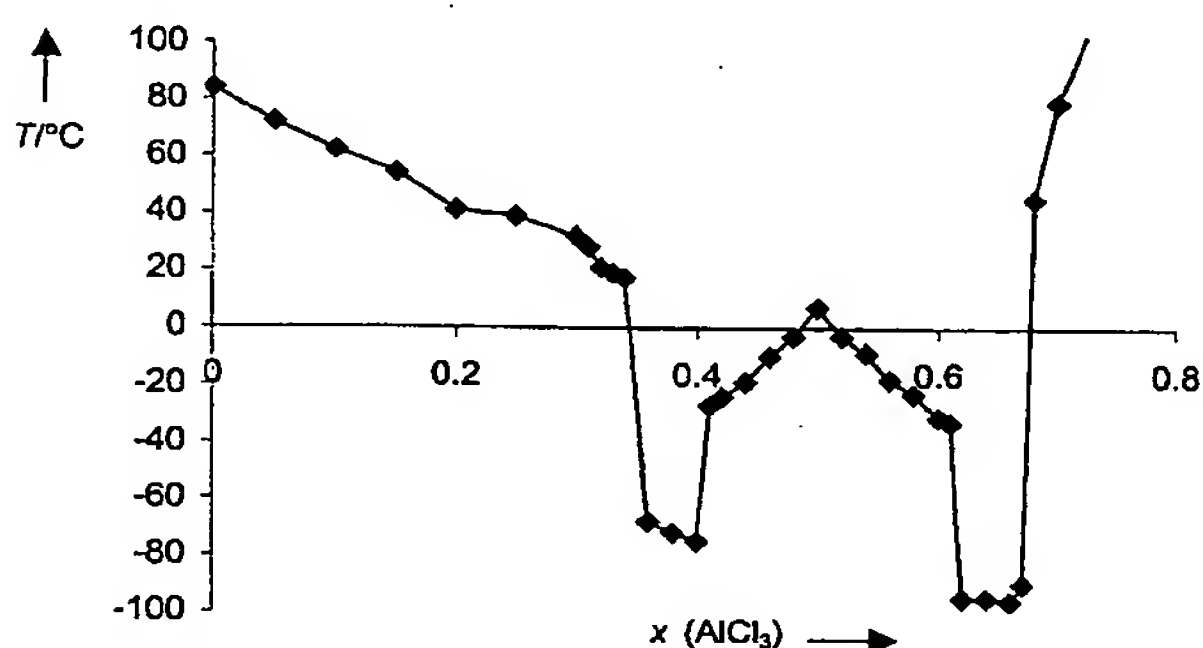
Auch das Anion hat einen Einfluss auf die Lage des Schmelzpunktes. Ein Vergleich der Schmelzpunkte unterschiedlicher Salze mit dem 1-Ethyl-3-methylimidazolium-(EMIM)-Ion verdeutlicht, dass in der Regel eine Vergrößerung des Anions bei gleicher Ladung zu einer weiteren Schmelzpunktniedrigung führt (Tabelle 5).

Bei ionischen Flüssigkeiten, die durch Reaktion eines Halogenids [Kation]⁺X⁻ mit einer Lewis-Säure MX_y gebildet werden, hat ferner das molare Verhältnis der beiden Eduktkomponenten einen Einfluss auf die Lage des Schmelzpunktes (Abbildung 2).^[40]

Tabelle 5. Einfluss unterschiedlicher Anionen auf den Schmelzpunkt von Imidazoliumsalzen.

Imidazoliumsalz	Schmp [°C]	Lit.
[EMIM]Cl	87	[6c]
[EMIM]NO ₂	55	[14]
[EMIM]NO ₃	38	[14]
[EMIM]AlCl ₄	7	[40]
[EMIM]BF ₄	6 ^[a]	[17d]
[EMIM]CF ₃ SO ₃	-9	[16a]
[EMIM]CF ₃ CO ₂	-14	[16a]

[a] Glasübergang.

Abbildung 2. Experimentelles Phasendiagramm des Systems [EMIM]Cl/AlCl₃ (EMIM = 1-Ethyl-3-methylimidazolium-Ion).

Wie bereits gezeigt wurde, liegt im System [EMIM]Cl/AlCl₃ nur in der exakten 1:1-Mischung beider Komponenten ein quasi-binäres System mit dem Anion AlCl₄⁻ vor. Die Tatsache, dass gerade bei dieser Zusammensetzung ein lokales Maximum der Schmelztemperatur auftritt, deutet auf einen schmelzpunktsenkenden Einfluss mehrerer Anionen in der ionischen Flüssigkeit hin.

3.2. Dampfdruck und thermische Stabilität

Ionische Flüssigkeiten haben keinen messbaren Dampfdruck. Dies ist aus verfahrenstechnischer Sicht ein großer Vorteil, da auf diese Weise die destillative Trennung eines Reaktionsgemisches als effektive Methode zur Produktabtrennung stark vereinfacht wird. Die bekannten Probleme durch Azeotropbildung zwischen Lösungsmittel und Produkten treten nicht auf.

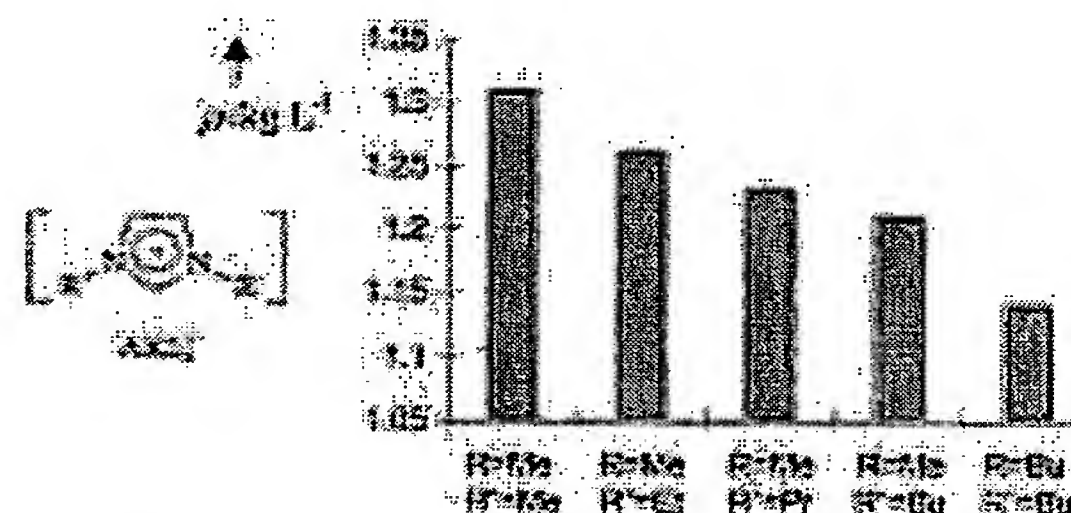
Die thermische Stabilität vieler ionischer Flüssigkeiten ist durch die Reaktivität ihrer Heteroatom-Kohlenstoff- bzw. ihrer Heteroatom-Wasserstoff-Bindungen begrenzt. Eine deutlich eingeschränkte thermische Stabilität weisen beispielsweise ionische Flüssigkeiten auf, die direkt durch Protonierung eines Amins oder Phosphans gebildet wurden. Viele Schmelzen mit Trialkylammonium-Ionen zersetzen sich (je nach Siedepunkt des jeweiligen Amins und der Säure) bereits bei Temperaturen von weniger als 80°C im Hochvakuum. Bei ionischen Flüssigkeiten, die durch Alkylierung eines Amins oder Phosphans gebildet wurden, hängt die Neigung zu thermischen Umalkylierungs- und Dealkylierungsreaktionen (Rückreaktion der Quaternisierung) stark von der Natur des Anions ab. Während für viele quartäre

Ammoniumsalze mit Chlorid-Ionen 150°C bereits als obere Grenze der Arbeitstemperatur angesehen werden muss, ist beispielsweise EMIM-Tetrafluoroborat bis rund 300°C^[41] und [EMIM][(CF₃SO₂)₂N] (Schmp. -3°C) sogar bis über 400°C stabil.^[16a] Im Unterschied zu Wasser und den meisten organischen Lösungsmitteln weisen einige ionische Flüssigkeiten folglich einen Flüssigkeitsbereich von über 400 Grad auf.

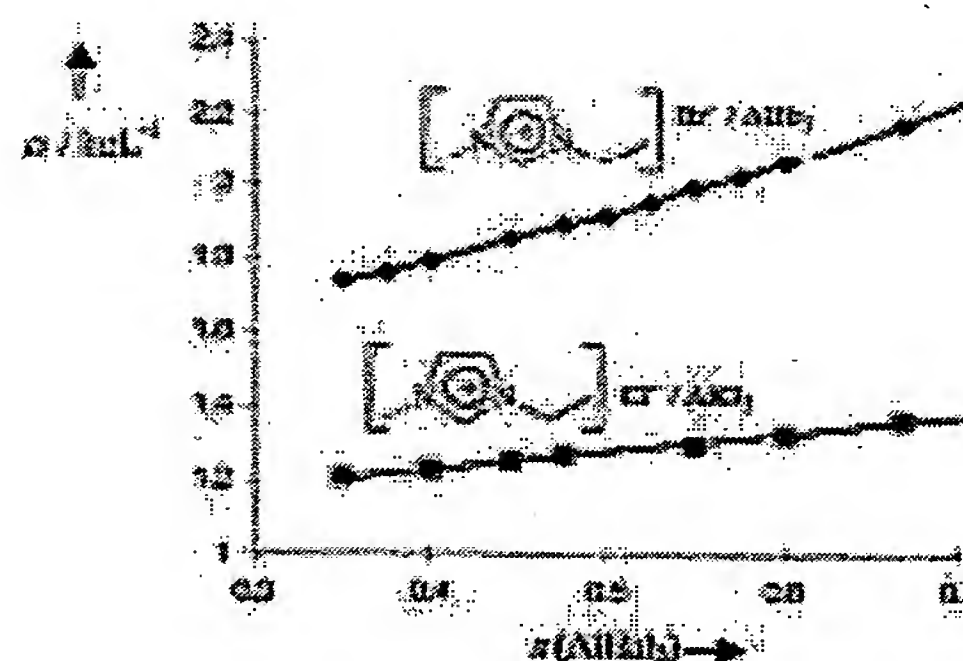
3.3. Dichte

Die Abhängigkeit der Dichte einer ionischer Flüssigkeit vom verwendeten Kation und Anion lässt sich eindrucksvoll am Beispiel der Chloroaluminat- und Bromoaluminat-Schmelzen verdeutlichen.

Beim Vergleich von Chloroaluminat-Schmelzen mit unterschiedlichen Kationen wird ein annähernd linearer Zusammenhang zwischen der Dichte und der Länge der N-Alkylkette am Imidazolium-Kation deutlich (Abbildung 3).^[40] Allgemeiner lässt sich folgern, dass die Dichte ähnlicher ionischer Flüssigkeiten umso niedriger liegt, je sperriger das organische Kation ist. Geringfügige Strukturveränderungen am Kation erlauben eine Feineinstellung der Dichte.

Abbildung 3. Abhängigkeit der Dichte ρ von 1,3-Dialkylimidazoliumtetrachloroaluminat-Schmelzen von der Art der beiden Alkylgruppen; Messtemperatur 60°C, $x(\text{AlCl}_3) = 0.5$.

Durch Variationen am Anion lassen sich in einigen Fällen deutlichere Effekte erzielen. Mit Bromoaluminat-Schmelzen gelingt es beispielsweise, Dichtebereiche zu erschließen, die für gebräuchliche organische Lösungsmittel eher ungewöhnlich sind (Abbildung 4).^[42] Auch die Dichtebestimmung von

Abbildung 4. Abhängigkeit der Dichte ρ von zwei EMIM-Tetrahalogenaluminat-Schmelzen vom Molenbruch an Aluminiumtrihalogenid bei 60°C.

ionischen Flüssigkeiten mit Trifluormethansulfonat(Triflat)- oder Trifluoracetat-Ionen bestätigt das allgemeinere Ergebnis, dass durch die Wahl des Anions ein gewisser Dichtebereich festgelegt wird, innerhalb dessen durch geeignete Wahl des Kations eine Feinabstufung möglich ist.^[16a]

3.4. Viskosität

Die Viskosität ionischer Flüssigkeiten wird wesentlich von deren Neigung zur Bildung von Wasserstoffbrückenbindungen und der Stärke der van-der-Waals-Wechselwirkungen bestimmt.^[16a]

Die Auswirkung der Wasserstoffbrückenbindung wird beispielsweise deutlich, wenn man die Viskositäten unterschiedlich zusammengesetzter Chloroaluminat-Schmelzen vergleicht (Abbildung 5).^[40] Der Viskositätsanstieg um mehr als

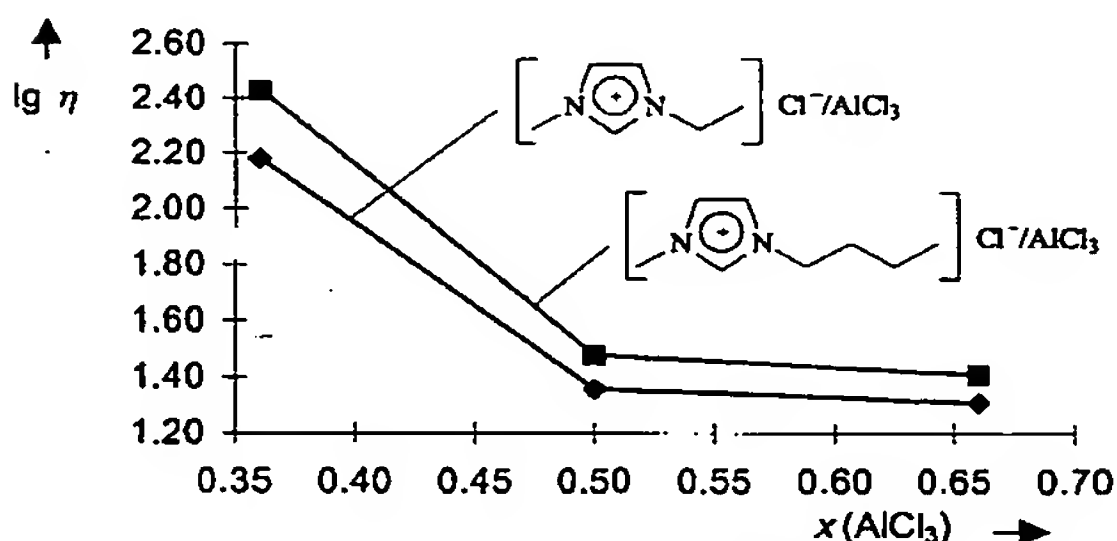


Abbildung 5. Abhängigkeit der dynamischen Viskosität η [cP] zweier 1,3-Dialkylimidazoliumtetrachloroaluminat-Schmelzen vom Molenbruch an Aluminiumtrichlorid bei 25 °C.

eine Zehnerpotenz bei ionischen Flüssigkeiten mit $x(\text{AlCl}_3) < 0.5$ beruht auf der Bildung von Wasserstoffbrückenbindungen zwischen den Wasserstoffatomen des Imidazolium-Kations und dem basischen Chlorid-Ion. Diese Aussage wird durch IR-^[43] und Röntgenspektroskopie,^[44] ROE-SY-NMR-Spektroskopie und theoretische Rechnungen^[45] gestützt. In aciden Gemischen liegen dagegen die Anionen AlCl_4^- und Al_2Cl_7^- vor, deren negative Ladung wesentlich besser verteilt ist. Dies führt zu schwächeren Wasserstoffbrückenbindungen und einer deutlich niedrigeren Viskosität.

Ein Vergleich der Viskositäten unterschiedlicher hydrophober ionischer Flüssigkeiten mit dem 1-*n*-Butyl-3-methylimidazolium(BMIM)-Ion verdeutlicht darüber hinaus das Zusammenspiel von van-der-Waals-Wechselwirkungen und Wasserstoffbrückenbindung (Tabelle 6).^[16a] Beim Übergang vom Triflat zum $n\text{-C}_4\text{F}_9\text{SO}_3^-$ -Ion sowie vom Trifluoracetat zum $n\text{-C}_3\text{F}_7\text{COO}^-$ -Ion wird ein deutlicher Viskositätsanstieg beobachtet. Offensichtlich führen die größeren van-der-Waals-Wechselwirkungen im Fall des $n\text{-C}_4\text{F}_9\text{SO}_3^-$ - und des $n\text{-C}_3\text{F}_7\text{COO}^-$ -Ions zu einer höheren Viskosität der ionischen Flüssigkeit. Beim Vergleich der Viskositäten von $[\text{BMIM}]\text{CF}_3\text{SO}_3$ und $[\text{BMIM}](\text{CF}_3\text{SO}_2)_2\text{N}$ erhält man dagegen trotz höherer van-der-Waals-Wechselwirkungen eine niedrigere

Tabelle 6. Dynamische Viskositäten η unterschiedlicher 1-*n*-Butyl-3-methylimidazolium(BMIM)-Salze bei 20 °C.

	Anion $[\text{A}]^-$	η [cP]
	CF_3SO_3^-	90
	$n\text{-C}_4\text{F}_9\text{SO}_3^-$	373
	CF_3COO^-	73
	$n\text{-C}_3\text{F}_7\text{COO}^-$	182
	$(\text{CF}_3\text{SO}_2)_2\text{N}^-$	52

Viskosität für die ionische Flüssigkeit mit dem $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ -Ion. In diesem Fall wird der eigentlich zu erwartende Viskositätsanstieg durch die fast vollständige Unterdrückung von Wasserstoffbrückenbindungen überkompensiert.

Auch die Struktur des Kations beeinflusst die Viskosität der ionischen Flüssigkeit. Die niedrigsten Viskositäten werden meist für Schmelzen mit dem EMIM-Ion erreicht, das eine ausreichende Beweglichkeit der Seitenkette mit einer niedrigen Molekülmasse verbindet. Längere oder fluorierte Alkylketten führen zu höheren Viskositäten auf Grund der höheren van-der-Waals-Wechselwirkungen.^[16a]

Die Viskosität ionischer Flüssigkeiten kann bereits durch geringe Temperaturerhöhung^[40, 46] oder durch die Zugabe von kleinen Mengen an organischen Cosolventien^[47] z. T. deutlich herabgesetzt werden.

3.5. Solvationsstärke und Löslichkeitseigenschaften

Besondere Aufmerksamkeit verdient die gezielte Einstellung eines gewünschten Löslichkeitsverhaltens der ionischen Flüssigkeit durch die geeignete Wahl von Kation und Anion.

Der Einfluss des Kations zeigt sich z. B. bei Untersuchungen zur Löslichkeit von 1-Octen in unterschiedlichen Toluolsulfonat(Tosylat)-Schmelzen (Abbildung 6).^[25] Man erkennt, dass mit zunehmend unpolarem Charakter des Kations die Löslichkeit von 1-Octen in der Schmelze deutlich zunimmt. Mit dem Methyltri-*n*-octylammoniumtosylat wird bereits ein einphasiges Reaktionsgemisch erhalten. Das Beispiel zeigt, dass durch die Variation von Alkylresten am Kation ionischer Flüssigkeiten eine stufenweise Regulierung der Löslichkeitseigenschaften möglich ist.

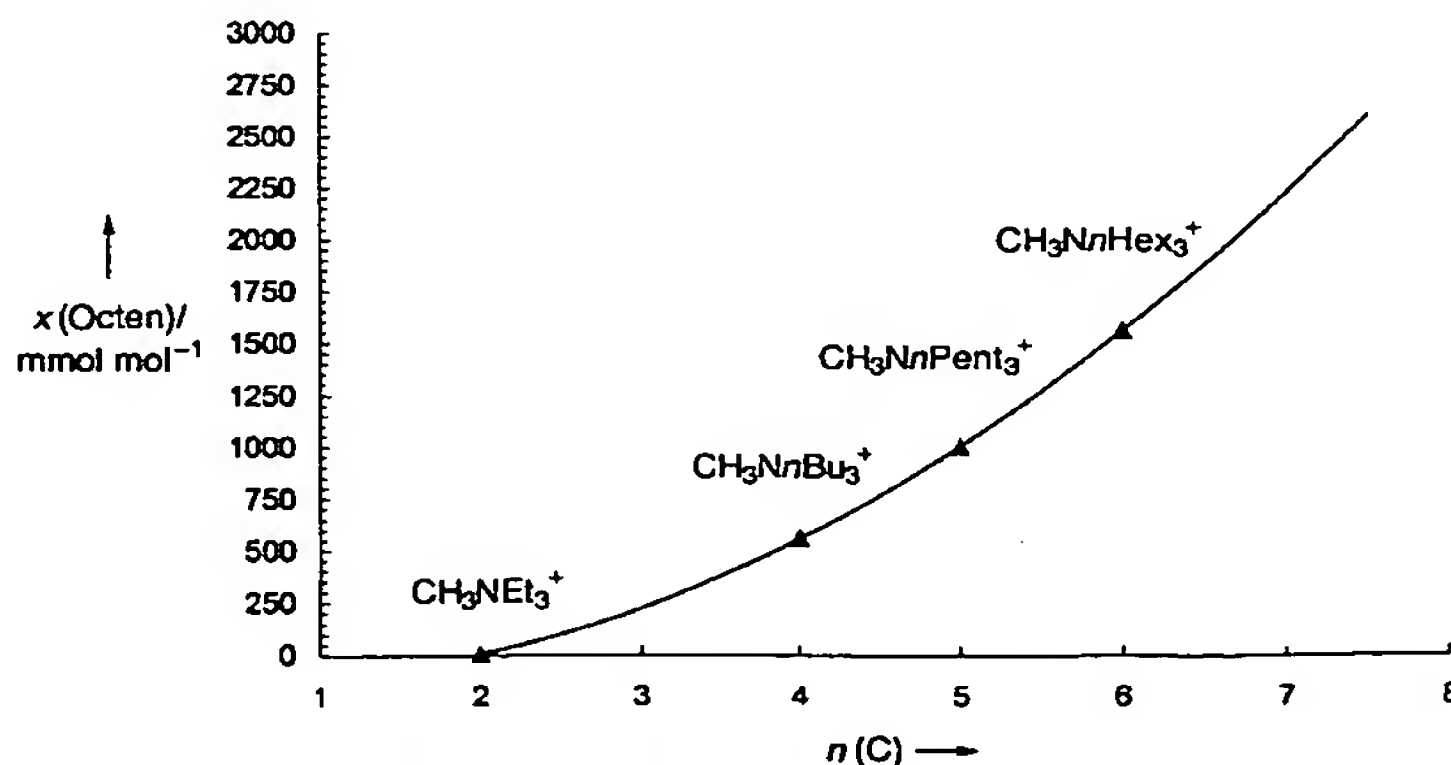


Abbildung 6. Löslichkeit von 1-Octen in vier Tri-*n*-alkylmethylammoniumtosylat-Schmelzen bei 80 °C. $n(\text{C})$ = Zahl der C-Atome des Alkylrestes.

Der Einfluss des Anions lässt sich eindrucksvoll am Beispiel der Wasserlöslichkeit unterschiedlicher Schmelzen mit dem BMIM-Ion veranschaulichen. Während z. B. [BMIM]Br, [BMIM]CF₃COO und [BMIM]CF₃SO₃ hervorragend wasserlöslich sind, bilden ionische Flüssigkeiten mit dem gleichen Kation, aber einem PF₆⁻- oder (CF₃SO₂)₂N⁻-Anion mit Wasser zweiphasige Gemische. Bei [BMIM](CF₃SO₂)₂N wird der Wassergehalt der ionischen Flüssigkeit bei 20°C mit lediglich 1.4 Massenprozent angegeben.^[16a]

Für ionische Flüssigkeiten, die eine Mischungslücke mit Wasser aufweisen, ergeben sich interessante Anwendungen im Bereich der Stofftrennung durch Flüssig-flüssig-Extraktion. Die Gruppe um Rogers untersuchte beispielsweise das Löslichkeitsverhalten unterschiedlicher Säuren und Basen im Zweiphasensystem Wasser/[BMIM]PF₆ in Abhängigkeit vom pH-Wert der Wasserphase.^[48] Die Ergebnisse zeigen interessanterweise eine erhöhte Löslichkeit der neutralen Substanzen in der ionischen Phase, während sich ionische Substrate bevorzugt in der wässrigen lösen. Die Autoren folgern, dass die ionische Flüssigkeit [BMIM]PF₆ hinsichtlich ihrer Löslichkeit in Wasser starke Ähnlichkeit zu organischen Lösungsmitteln aufweist. In extraktiven Verfahren zur Stofftrennung halten sie die Substitution flüchtiger organischer Lösungsmittel durch geeignete ionische Flüssigkeiten für viel versprechend.

Viele ionische Flüssigkeiten sind mit organischen Lösungsmitteln vollständig mischbar, wenn deren Dielektrizitätskonstante einen charakteristischen Grenzwert übersteigt. Die Lage dieses Grenzwertes scheint für jede Kation/Anion-Kombination spezifisch zu sein (Tabelle 7).^[16a]

Bemerkenswert ist auch die Löslichkeit von überkritischem CO₂ (scCO₂) in [BMIM]PF₆, die kürzlich von der Gruppe um Brennecke untersucht wurde.^[49] Im zweiphasigen System scCO₂/[BMIM]PF₆ lösen sich bei 80 bar CO₂-Druck rund 60 Mol-% CO₂ in der ionischen Flüssigkeit, deren Volumen dabei aber nur um 10–20% zunimmt. Als erste Anwendung dieses interessanten Zweiphasensystems untersuchten die Autoren die Extraktion von Naphthalin aus der ionischen Flüssigkeit. Dabei gelang eine vollständige Rückgewinnung des Naphthalins, ohne dass der Extrakt mit der ionischen Flüssigkeit kontaminiert wurde.

Ohne Zweifel liegt in der geschickten Nutzung der außerordentlichen Löslichkeitseigenschaften ionischer Flüssigkeiten ein Schlüssel zum erfolgreichen Einsatz dieser neuartigen Lösungsmittel. Es sind jedoch weitere systematische Untersuchungen nötig, um hier das Potential voll ausschöpfen zu können.

Einen viel versprechenden Ansatz bietet beispielsweise die Untersuchung der Polarität ionischer Flüssigkeiten: Die

Polarität eines Lösungsmittels wird üblicherweise auf rein empirischem Weg bestimmt. Man untersucht dabei einen gut bekannten, leicht messbaren und stark solvensabhängigen Prozess in einer großen Zahl unterschiedlicher Lösungsmittel, z. B. das Absorptionsverhalten eines solvatochromen Farbstoffs. Aus den ermittelten Absorptionsmaxima werden empirische Parameter der Lösungsmittelpolarität abgeleitet, die ein umfassenderes Maß des Solvatationsvermögens eines Lösungsmittels darstellen als seine einzelnen physikalischen Konstanten.^[50] Unter den zahlreichen, empirischen Polaritätsskalen hat sich insbesondere die 1963 von Dimroth et al. eingeführte^[51] und von Reichhardt et al. seit 1971 weiterentwickelte $E_{(T)}(30)$ -Scala bewährt, die auf der Solvatochromie eines Pyridinium-*N*-phenolat-Betainfarbstoffs basiert.^[52] Diese Methode konnte auch erfolgreich zur Bestimmung der Polarität einer kleinen Zahl ionischer Flüssigkeiten genutzt werden. Die dabei erhaltenen Ergebnisse belegen die beachtliche Variationsbreite der Lösungsmittelpolarität ionischer Flüssigkeiten. Während beispielsweise die Polarität von Tetra-*n*-hexylammoniumbenzoat mit einem $E_{(T)}(30)$ -Wert von 0.41 im Bereich der Polarität von DMF liegt,^[53] wurde für Ethylammoniumnitrat ein $E_{(T)}(30)$ -Wert von 0.95 bestimmt, was einer Polarität zwischen der von CF₃CH₂OH und Wasser entspricht.^[4, 54] Die Untersuchung von [BMIM]PF₆ nach dem gleichen Verfahren ergab einen $E_{(T)}(30)$ -Wert, der auf eine Polarität schließen lässt, die ähnlich hoch ist wie die von Methanol.^[55]

Allerdings haben jüngste Untersuchungen der Gruppe um Armstrong die Frage aufgeworfen, inwieweit die chemische Natur des solvatochromen Farbstoffs Einfluss auf das Ergebnis der Polaritätsuntersuchung einer ionischen Flüssigkeit nimmt. Sie belegten GC-Säulen mit unterschiedlichen ionischen Flüssigkeiten und verglichen die Retentionszeiten einer großen Zahl von Testsubstanzen.^[56] Dabei erhielten sie Hinweise auf ein unterschiedliches Polaritätsverhalten von ionischen Flüssigkeiten gegenüber polaren und unpolaren Verbindungen. [BMIM]PF₆ verhielt sich beispielsweise gegenüber unpolaren Substanzen (z. B. *n*-Octan) wie eine unpolare stationäre Phase, während Testsubstanzen mit Protonendoneigenschaften sehr lange Retentionszeiten aufwiesen. Die Autoren sprechen von einem dualen Polaritätsverhalten der untersuchten ionischen Flüssigkeit.

Leider ist die Zahl systematischer Arbeiten zur Polarität ionischer Flüssigkeiten noch sehr begrenzt. Um für eine gegebene Lösungsmittelanwendung eine geeignete ionische Flüssigkeit zu finden, sind weitere Untersuchungen, die effiziente Auswahlkriterien an die Hand geben, sehr wünschenswert.

Tabelle 7. Mischbarkeit unterschiedlicher ionischer Flüssigkeiten mit 1-Ethyl-3-methylimidazolium(EMIM)-Ion in organischen Lösungsmitteln mit der Dielektrizitätskonstanten ϵ .^[a]

Lösungsmittel	[EMIM]CF ₃ SO ₃	[EMIM]CF ₃ COO	[EMIM] <i>n</i> -C ₃ F ₇ COO	[BMIM]CF ₃ COO	[BMIM] <i>n</i> -C ₃ F ₇ COO
CH ₂ Cl ₂ (ϵ = 8.93)	m	m	m	m	m
THF (ϵ = 7.58)	m	m	m	m	m
Ethylacetat (ϵ = 6.02)	m	tm	tm	m	m
Toluol (ϵ = 2.38)	nm	nm	nm	nm	nm
1,4-Dioxan (ϵ = 2.01)	nm	nm	nm	nm	nm

[a] m: mischbar; tm: teilweise mischbar; nm: nicht mischbar.

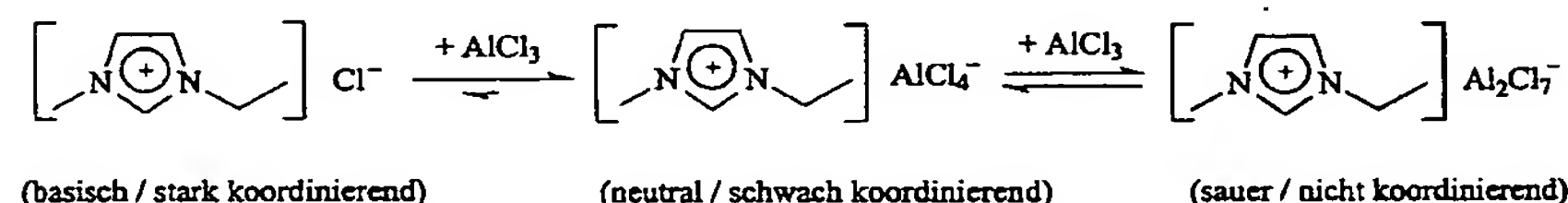
3.6. Acidität und Koordinationsfähigkeit

Die Acidität und die koordinativen Eigenschaften einer ionischen Flüssigkeit werden wesentlich von der Natur des verwendeten Anions geprägt. Zwischen „stark basisch/stark koordinierend“ und „stark sauer/praktisch nicht koordinierend“ können durch die Auswahl eines geeigneten Anions zahlreiche Zwischenstufen eingestellt werden (Tabelle 8).^[30]

Tabelle 8. Koordinative Eigenschaften unterschiedlicher Anionen.

basisch/stark koordinierend	Acidität/Koordination neutral/schwach koordinierend	sauer/nicht koordinierend
Cl ⁻	AlCl ₄ ⁻	Al ₂ Cl ₇ ⁻
Ac ⁻	CuCl ₂ ⁻	Al ₃ Cl ₁₀ ⁻
NO ₃ ⁻		
SO ₄ ²⁻	SbF ₆ ⁻	Cu ₂ Cl ₃ ⁻
	BF ₄ ⁻	
	PF ₆ ⁻	Cu ₃ Cl ₄ ⁻

Noch einmal sei hier auf die Systeme hingewiesen, bei denen durch Zugabe einer Lewis-Säure (z.B. AlCl₃) aus einem basischen Anion (z.B. Cl⁻) ein neutrales (z.B. AlCl₄⁻) oder ein saures Anion (z.B. Al₂Cl₇⁻) gebildet wird. In Schema 3 ist dieses Verhalten am Beispiel einer EMIM-

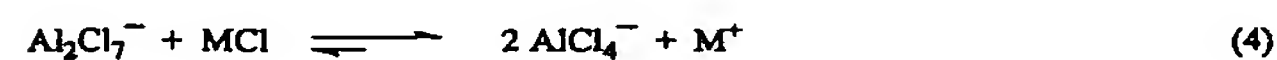


Schema 3. Steuerung der Acidität ionischer Flüssigkeiten über das Verhältnis von Halogenid zu Lewis-Säure am Beispiel einer EMIM-Chloroaluminat-Schmelze.

Chloroaluminat-Schmelze dargestellt. Chloroaluminat-Schmelzen bezeichnet man daher als basisch, wenn ihr molarer Anteil an AlCl₃ kleiner als 0.5 ist. Bei einem AlCl₃-Anteil von exakt 0.5, bei dem praktisch nur das Anion AlCl₄⁻ vorliegt, spricht man von einer neutralen Schmelze.^[22a] Schließlich bezeichnet man eine Chloroaluminat-Schmelze als acide, falls der AlCl₃-Anteil größer als 0.5 ist. In solchen aciden Schmelzen liegen die Anionen Al₂Cl₇⁻ und Al₃Cl₁₀⁻ vor, die wie sehr starke Lewis-Säuren wirken.^[27]

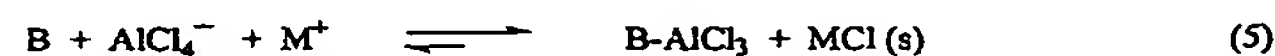
Zwei weitere Phänomene im Bereich der Säure/Base-Chemie ionischer Flüssigkeiten verdienen Beachtung. Es handelt sich dabei um die so genannte „latente Acidität“ und um die „Superacidität“ von Protonen in ionischen Flüssigkeiten.

Die latente Acidität ionischer Flüssigkeiten tritt bei der Zugabe schwacher Basen zu neutral gepufferten Chloroaluminat-Schmelzen auf. Solche Schmelzen entstehen, wenn man z.B. ein Alkalimetallchlorid (MCl) im Überschuss zu einer aciden Chloroaluminat-Schmelze gibt.^[57] MCl reagiert dabei nach Gleichung (4) mit dem aciden Chloroaluminat-Dimer



bis zur Neutralität der Schmelze. Von einer gepufferten Schmelze spricht man, weil bei einer erneuten Zugabe der

Säure AlCl₃ die Neutralität der Schmelze durch Reaktion mit dem überschüssigen Alkalimetallchlorid erhalten bleibt. Die latente Acidität dieser an sich neutralen Systeme macht sich dagegen bemerkbar, wenn man eine schwache Base (B) wie *N,N*-Dimethylanilin, Pyrrol oder Acetylferrocen zugibt.^[58] Es bildet sich unter Ausfällung des Alkalimetallchlorids MCl das Addukt aus der zugegebenen Base und AlCl₃ [Gl. (5)].



Ohne überschüssige Alkalimetallkationen tritt die Reaktion nicht auf. Die latente Acidität unterschiedlicher ionischer Flüssigkeiten konnte bereits quantitativ bestimmt werden.^[59] In unserer Gruppe wurden ionische Flüssigkeiten mit latenter Acidität erfolgreich als Lösungsmittel in der Ni-katalysierten Oligomerisierung von 1-Buten eingesetzt (siehe Abschnitt 4.8).^[60]

Daneben ist die Superacidität von Protonen in einigen ionischen Flüssigkeiten bemerkenswert. Sie tritt auf, wenn man starke Mineralsäuren in aciden ionischen Flüssigkeiten löst.^[61] Smith und Mitarbeiter haben die Acidität solcher Protonen in ionischen Flüssigkeiten untersucht, indem sie mit einer Lösung von HCl-Gas in aciden [EMIM]Cl/AlCl₃-Schmelzen Arylverbindungen protonierten. Mit Hilfe UV-spektroskopischer Methoden konnte die Acidität der Protonen in der Schmelze quantitativ bestimmt werden.^[61a] In Abhängigkeit von der Acidität der Schmelze ergaben sich Säurestärken, die deutlich über der von 100-proz. Schwefelsäure liegen (Abbildung 7).^[62]

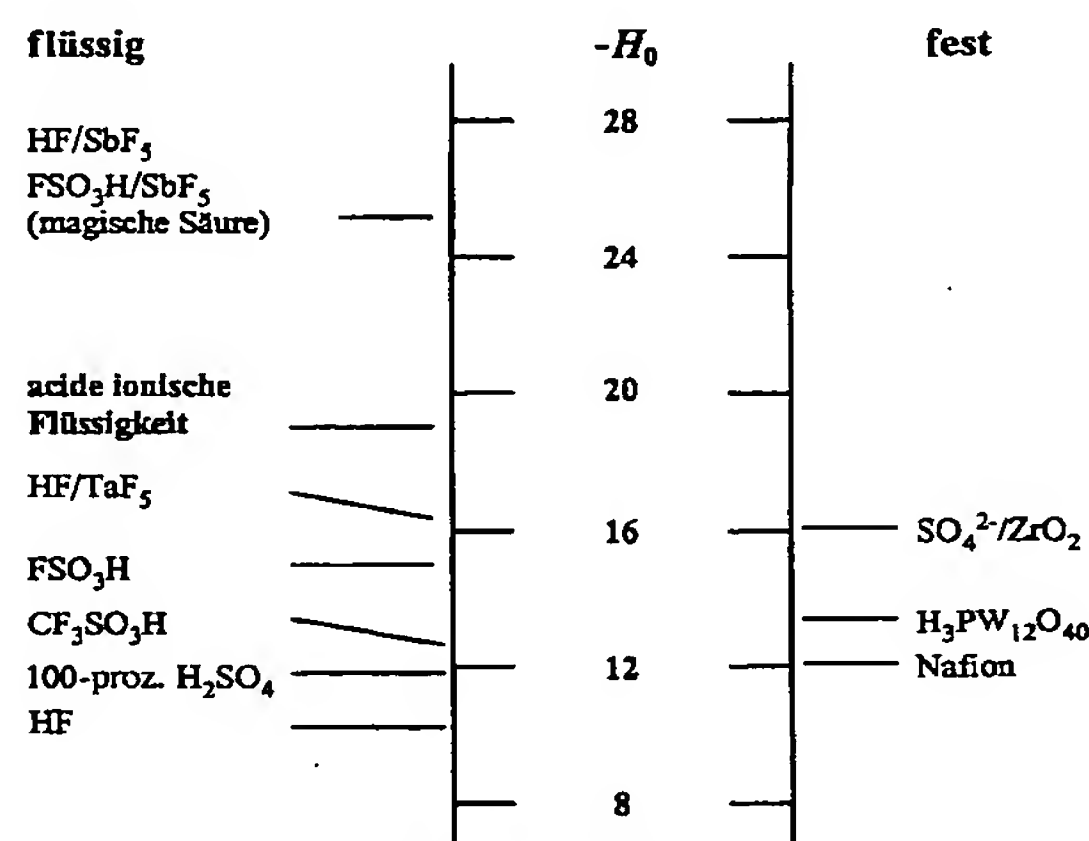


Abbildung 7. Vergleich der Säurestärken superacider ionischer Flüssigkeiten mit denen herkömmlicher Supersäuren.

Die superaciden Eigenschaften der Protonen in aciden Chloroaluminat-Schmelzen werden durch eine Reaktion zwischen dem gelösten HCl und den aciden Spezies der Schmelze erklärt, wodurch extrem schwach solvatisierte

und damit sehr reaktive Protonen freigesetzt werden [Gl. (6)].



Im Unterschied zu herkömmlichen supersauren Systemen sind superacide ionische Flüssigkeiten wesentlich einfacher und sicherer zu handhaben.^[61a] Sie könnten daher für einige Anwendungen viel versprechende Alternativen zu den bisher eingesetzten Supersäuren sein.

Schließlich soll darauf hingewiesen werden, dass auch das Kation einer ionischen Flüssigkeit Einfluss auf die Acidität des Systems nehmen kann. So wird beispielsweise dem Imidazolium-Ion selbst auch eine schwache Lewis-Acidität zugeschrieben. Die katalytische Wirkung von Imidazoliumbromid-Schmelzen in Diels-Alder-Reaktionen wird unter anderem auf diese geringe Acidität des Imidazolium-Ions zurückgeführt.^[63] Außerdem weist das H-Atom in 2-Position eines Imidazolium-Ions eine merkliche Brønsted-Acidität auf.^[64] Für Reaktionen mit Übergangsmetallkomplexen ist dies von besonderer Bedeutung, da in Gegenwart von Basen in diesen Systemen in situ Carbenkomplexe entstehen können.^[65]

3.7. Handhabbarkeit und Verfügbarkeit

Die Handhabbarkeit ionischer Flüssigkeiten hängt wesentlich von der Hydrolysestabilität des Anions ab. Während beispielsweise ionische Flüssigkeiten mit Nitrat-, Benzolsulfonat- oder [Bis(trifluormethylsulfonyl)]amid-Ionen luft- und wasserstabil sind, ja sogar in Wasser synthetisiert werden können, müssen Systeme mit Chloroaluminat-Anionen als extrem hygroskopisch und hydrolyselabil eingestuft werden. Erschwerend kommt hinzu, dass Wasserspuren in Chloroaluminat-Schmelzen mit den Anionen der Schmelze unter Freisetzung von superaciden Protonen reagieren. Letztere führen zu unerwünschten Nebenreaktionen und weisen ein erhebliches Korrosionspotential auf. Da eine vollständig wasserfreie Herstellung von Chloroaluminat-Schmelzen schwierig ist (eine ausführliche Behandlung protischer und oxidischer Verunreinigungen in Chloroaluminat-Schmelzen findet sich in Weltons Übersichtsartikel^[19]) wird man von Fall zu Fall entscheiden müssen, welches Maß an Verunreinigungen in diesen Systemen für die jeweilige Anwendung tolerierbar ist. Als Fazit bleibt, dass die Handhabbarkeit und Stabilität ionischer Flüssigkeiten nicht pauschal bewertet werden kann, sondern insbesondere von der Natur des verwendeten Anions abhängt.

Bis vor kurzem war die kommerzielle Verfügbarkeit von ionischen Flüssigkeiten sehr begrenzt. Nur wenige Systeme konnten über den Chemikalienhandel in Kleinmengen (bis 25 g) bezogen werden.^[66] Seit Ende 1999 sind zahlreiche ionische Flüssigkeiten auch in größeren Mengen (bis 5 Liter) kommerziell erhältlich.^[67] Bei wachsender Nachfrage ist davon auszugehen, dass insbesondere die Produzenten der Vorstufen (etwa der Amine) als Anbieter für ionische

Flüssigkeiten auftreten werden. In diesem Fall kann auch von deutlich sinkenden Preisen ausgegangen werden.

In diesem Zusammenhang soll darauf hingewiesen werden, dass ionische Flüssigkeiten nach ihrer Verwendung meist einfach zurückgewonnen, gegebenenfalls gereinigt und mehrfach eingesetzt werden können. Die Kosten für eine ionische Flüssigkeit sind also im Idealfall als einmalige Investition zu betrachten.

3.8. Umweltaspekte

In jüngster Zeit werden ionische Flüssigkeiten häufig als aussichtsreiche Lösungsmittel für „saubere Prozesse“ und eine „Grüne Chemie“ diskutiert.^[36, 68] Diese beiden Schlagwörter stehen für aktuelle Bestrebungen, die Menge an Neben- und Koppelprodukten, aber auch den Verbrauch an Lösungsmitteln und Katalysatoren in chemischen Prozessen zu verringern. Vor allem in Bezug auf den Lösungsmittel- und Katalysatorverbrauch kann die Verwendung von ionischen Flüssigkeiten einen Beitrag leisten.

Im Unterschied zu flüchtigen, organischen Lösungs- und Extraktionsmitteln haben ionische Flüssigkeiten keinen messbaren Dampfdruck. Ein Verlust des Lösungsmittels durch Verdampfung tritt daher nicht auf. Ökologische und sicherheitstechnische Probleme, die durch das Ausgasen flüchtiger, organischer Lösungsmittel auftreten, lassen sich ebenfalls durch die Verwendung eines nichtflüchtigen, ionischen Reaktionsmediums vermeiden.

In Bezug auf die angestrebte Verringerung des Katalysatorverbrauchs ergeben sich durch die Verwendung ionischer Flüssigkeiten zwei Ansatzpunkte: Zum einen bieten die speziellen Löslichkeitseigenschaften des ionischen Reaktionsmediums häufig die Chance einer zweiphasigen Reaktionsführung. Unter Nutzung der Mischungslücke zwischen ionischer Katalysatorphase und Produkten kann in diesem Fall der Katalysator effektiv vom Produkt abgetrennt und mehrfach eingesetzt werden. Zum anderen erlaubt die nichtflüchtige Natur des ionischen Lösungsmittels eine effektive Produktabtrennung durch Destillation. Auch hier besteht die Möglichkeit, die isolierte, ionische Katalysatorphase wiederzuverwenden. In beiden Fällen wird die Gesamtkativität des eingesetzten Katalysators gesteigert und der Katalysatorverbrauch bezogen auf das hergestellte Produkt herabgesetzt.

Vor allem in Prozessen mit supersauren Katalysatoren könnte aus ökologischen und sicherheitstechnischen Gründen die Verwendung ionischer Flüssigkeiten Bedeutung erlangen. Die Substitution von HF durch nichtflüchtige superacide ionische Flüssigkeiten ist diesbezüglich eine viel versprechende Alternative.

Mittlerweile wird durch eine Vielzahl von Reaktionsbeispielen (siehe dazu Abschnitt 4) belegt, dass die Verwendung ionischer Flüssigkeiten tatsächlich zu unter ökologischen Gesichtspunkten stark verbesserten Verfahren führen kann. Wir halten daher aus heutiger Sicht ihre Einordnung als „Green Solvents“ für gerechtfertigt. Gleichwohl muss an dieser Stelle darauf hingewiesen werden, dass toxikologische und ensorgungstechnische Aspekte bisher weitgehend unerforscht geblieben sind.

4. Ionische Flüssigkeiten als Lösungsmittel für Übergangsmetall-katalysierte Reaktionen

Ionische Flüssigkeiten können metallorganische Verbindungen lösen und stehen daher als Lösungsmittel für homogen katalysierte Reaktionen zur Verfügung. In Abhängigkeit von den koordinativen Eigenschaften des verwendeten Anions (siehe Abschnitt 3.6) ist die ionische Flüssigkeit dabei als Cokatalysator oder als inertes Lösungsmittel zu betrachten.

So verhalten sich beispielsweise ionische Flüssigkeiten mit Tetrafluoroborat- und Hexafluorophosphat-Ionen in den meisten Reaktionen (Ausnahmen siehe z. B. in Abschnitt 4.5) als inerte Lösungsmittel. In diesem Fall stellt die ionische Flüssigkeit lediglich ein schwach koordinierendes, polares Medium für den Übergangsmetallkatalysator dar, das sich durch spezielle Löslichkeitseigenschaften gegenüber den Edukten/Produkten auszeichnen kann. Häufig sind Kombinationen von Lösungsmitelegenschaften realisierbar, die mit traditionellen polaren, organischen Lösungsmitteln oder mit Wasser nicht erreicht werden können.

Bei ionischen Flüssigkeiten, die durch Reaktion eines Halogenids mit einer Lewis-Säure gebildet werden (z. B. Chloroaluminat- oder Chlorostannat-Schmelzen), spielt die ionische Flüssigkeit dagegen in der Regel die Rolle eines Cokatalysators. Grund dafür ist die stets (wenigstens latent) vorhandene Lewis-Acidität oder Lewis-Basizität, die zu starken Wechselwirkungen mit dem Katalysatorkomplex führt. In vielen Fällen nutzt man die Lewis-Acidität einer ionischen Flüssigkeit, um neutrale Katalysatorvorstufen in situ in die kationische, aktive Katalysatorverbindung zu überführen. Beispiele hierfür sind die Aktivierung von $[\text{Cp}_2\text{TiCl}_2]$ ^[13] in aciden Chloroaluminat-Schmelzen sowie die Aktivierung von $[(\text{PR}_3)_2\text{PtCl}_2]$ in ionischen Flüssigkeiten mit Chlorostannat-Ionen^[31c] [Gl. (7) und (8)].



Die Gründe, ionische Flüssigkeiten als Alternativlösungsmittel in bekannten Übergangsmetall-katalysierten Reaktionen zu untersuchen, sind vielfältig. Neben dem verfahrenstechnischen Vorteil ihrer nichtflüchtigen Natur, ist die Untersuchung neuer Zweiphasenreaktionen mit ionischer Katalysatorphase besonders interessant. Dabei können durch unterschiedliche Kation/Anion-Kombination die Löslichkeitseigenschaften so gezielt eingestellt werden, dass eine systematische Optimierung der Zweiphasenreaktion z. B. hinsichtlich der Produktselektivität möglich wird: Die bevorzugte Löslichkeit nur eines Reaktanten in der Katalysatorphase sowie die In-situ-Extraktion eines Reaktionsintermediates aus der Katalysatorphase sind attraktive Möglichkeiten zur Selektivitätssteuerung in Mehrphasensystemen. Schließlich besteht vor allem bei der Verwendung ionischer Katalysatorkomplexe eine gute Chance, dass sich ionische Flüssigkeiten als überlegene Lösungsmittel im Vergleich zu

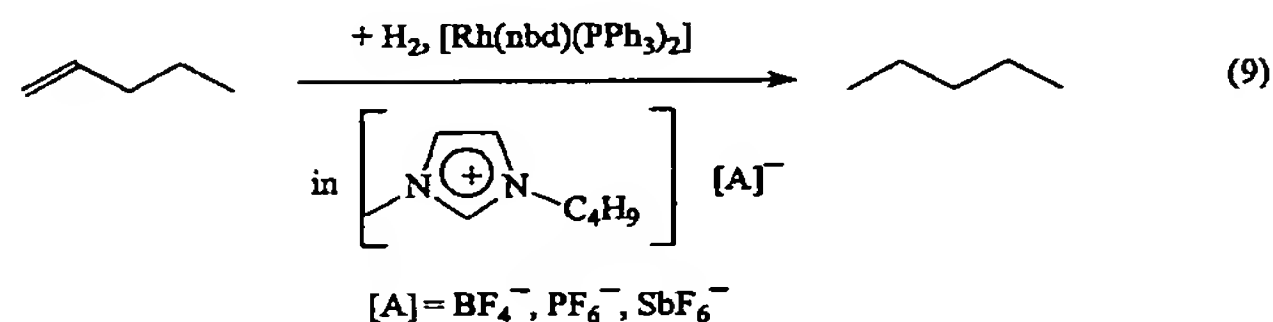
Wasser oder polaren organischen Lösungsmitteln erweisen. Deutliche Aktivitäts- und Stabilitätssteigerungen sind in diesen Fällen möglich.

In unserer Gruppe untersuchen wir seit 1995 die Reaktivität ionischer Lösungen von Übergangsmetallkatalysatoren und führen zurzeit Arbeiten zur Hydrierung, Hydroformylierung und Oxidation sowie zur Oligomerisierung von funktionalisierten und nichtfunktionalisierten Alkenen durch.

Im Folgenden soll anhand ausgewählter Reaktionen ein Überblick über die jüngsten Entwicklungen auf dem Gebiet der Übergangsmetallkatalyse in ionischen Flüssigkeiten gegeben werden.

4.1. Hydrierungen

Die ersten erfolgreichen Hydrierungsexperimente in bei Raumtemperatur flüssigen ionischen Flüssigkeiten wurden 1995 von den Gruppen um de Souza^[32] und Chauvin^[15] durchgeführt. Die Gruppe um de Souza untersuchte die Rh-katalysierte Hydrierung von Cyclohexen in BMIM-Tetrafluoroborat. Die Gruppe um Chauvin löste den kationischen „Osborn-Komplex“ $[\text{Rh}(\text{nbd})(\text{PPh}_3)_2]\text{PF}_6$ (nbd = Norbornadien) in unterschiedlichen ionischen Flüssigkeit mit schwach koordinierenden Anionen (z. B. PF_6^- , BF_4^- und SbF_6^-) und setzten die erhaltene ionische Katalysatorlösung gemäß Gleichung (9) zur zweiphasigen Hydrierung von 1-Penten ein.



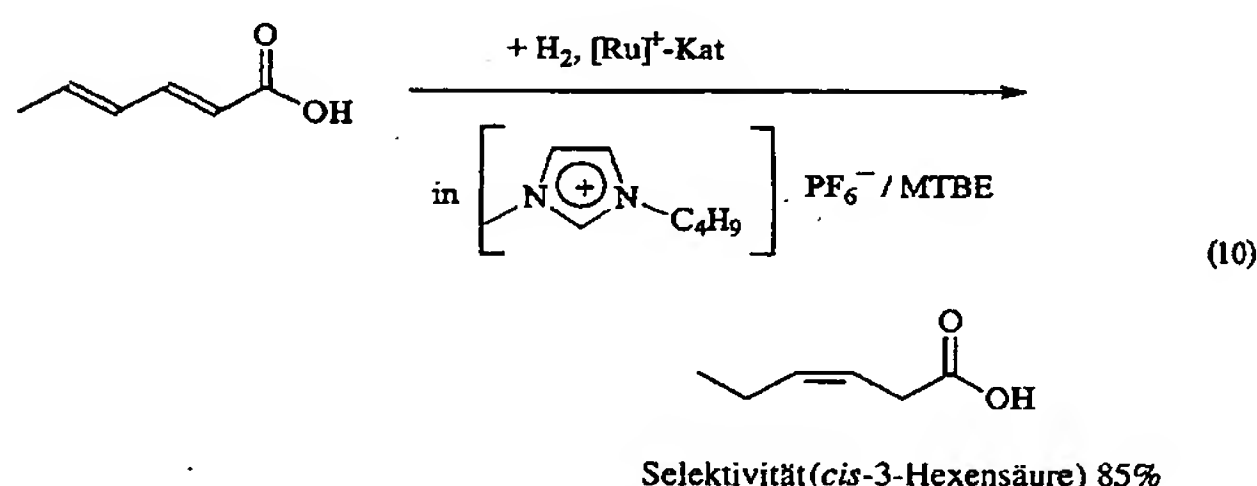
Obwohl sich die Reaktanten nur begrenzt in der Katalysatorphase lösen, ist die Hydriergeschwindigkeit in $[\text{BMIM}]\text{SbF}_6$ fast fünfmal höher als bei der entsprechenden Reaktion in Aceton. Alle eingesetzten ionischen Katalysatorlösungen konnten wiederholt verwendet werden. Der Verlust an Rhodium durch Ausbluten in die organische Phase lag unterhalb der Nachweisgrenze von 0.02 %. Diese Ergebnisse sind für den gesamten Bereich der Zweiphasenkatalyse von Bedeutung, da es hier zum ersten Mal gelang, einen Rhodiumkatalysator in einer polaren Phase zu „immobilisieren“ ohne einen eigens dafür entworfene Liganden einzusetzen.

Außerdem gelang Chauvin et al. die selektive Hydrierung von Cyclohexadien zu Cyclohexen unter Nutzung des mehrphasigen Reaktionssystems.^[15] Da die Löslichkeit von Cyclohexadien in $[\text{BMIM}]\text{SbF}_6$ rund fünfmal höher ist als die von Cyclohexen, konnte Letzteres in einer Selektivität von 98 % bei 96 % Umsatz erhalten werden. Allerdings beobachteten die Autoren eine vollständige Unterdrückung der Hydrieraktivität des Rh-Katalysators, wenn die verwendete ionische Flüssigkeit Cl^- -Verunreinigungen enthielt.

Auch die Rhodium- und Cobalt-katalysierte Hydrierung von Butadien und 1-Hexen^[32, 69] sowie die Ru-katalysierte

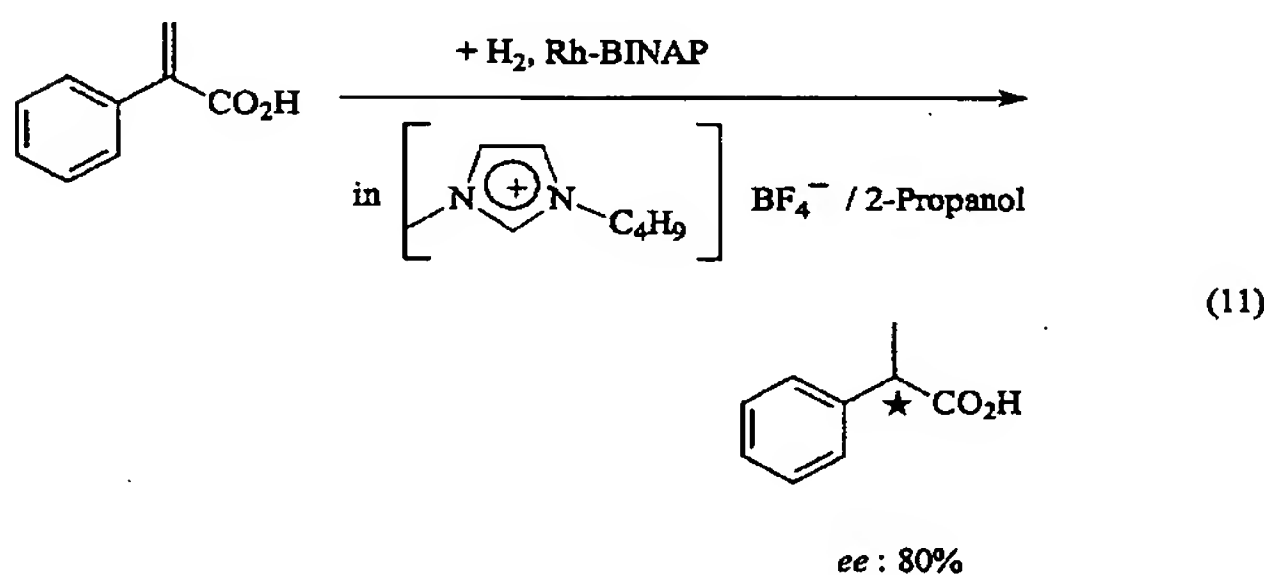
Hydrierung von Arenen^[18c] und von Acrylonitril-Butadien-Copolymeren^[70] wurden bereits erfolgreich in ionischen Flüssigkeiten durchgeführt.

Eine stereoselektive Hydrierung in ionischen Flüssigkeiten gelang vor kurzem an unserem Institut. Aufbauend auf Arbeiten im Zweiphasensystem Wasser/*n*-Heptan^[71] konnte die Ruthenium-katalysierte Hydrierung von Sorbinsäure zu *cis*-3-Hexensäure gemäß Gleichung (10) im System [BMIM]PF₆/MTBE (MTBE = Methyl-*tert*-butylether) erfolgreich durchgeführt werden.^[72]



Gegenüber anderen polaren Lösungsmitteln (z.B. Glykol) beobachtet man bei der Reaktion in der ionischen Flüssigkeit eine mehr als dreimal höhere Aktivität bei ähnlicher Selektivität zugunsten der *cis*-3-Hexensäure. Nach der Reaktion konnte die ionische Katalysatorlösung durch Phasentrennung zurückgewonnen werden und mehrfach wiederverwendet werden.

Enantioselektive Hydrierungen in ionischen Flüssigkeiten sind ebenfalls möglich. Die Gruppe um Chauvin hydrierte α -Acetamidozimtsäure in Gegenwart eines [Rh(cod)((-)-diop)]-Katalysators (cod = Cycloocta-1,3-dien; diop = 4,5-Bis[(diphenylphosphanyl)methyl]-2,2-dimethyl-1,3-dioxolan-4,5-diol in einer [BMIM]SbF₆-Schmelze mit 64 % *ee* zu (*S*)-Phenylalanin.^[15] Mit bis zu 80 % *ee* konnte die Gruppe um Dupont in [BMIM]BF₄-Schmelzen 2-Arylacrylsäuren mit Ru-BINAP-Katalysatoren^[73] (BINAP = 2,2'-Bis(diphenylphosphanyl)-1,1'-binaphthyl) zu (*S*)-2-Phenylpropionsäure umsetzen [Gl. (11)]. Beide Reaktionen wurden mit Hilfe eines



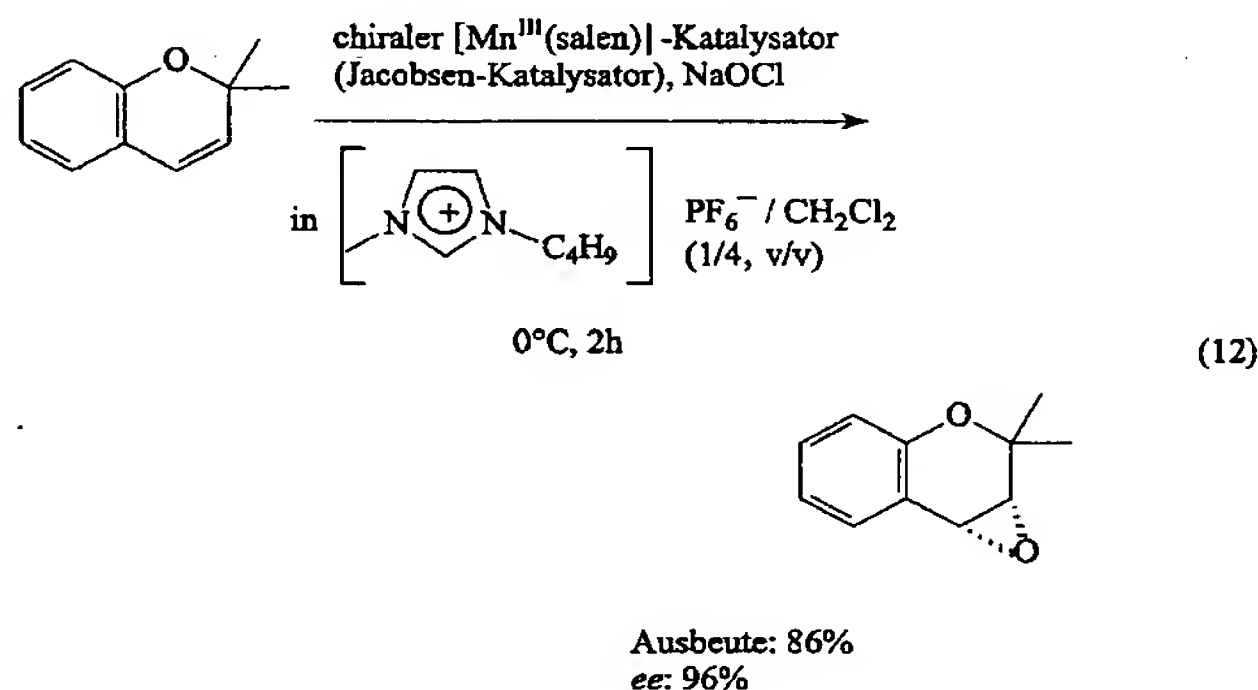
weiteren organischen Lösungsmittels (z.B. *i*PrOH) zweiphasig durchgeführt. Der Katalysator konnte nach dem Abdekantieren der Hydrierprodukte erneut mit gleicher Aktivität und Enantioselektivität eingesetzt werden.

Generell sind Übergangsmetall-katalysierte Hydrierungen in ionischen Flüssigkeiten als besonders aussichtsreich ein-

zuschätzen: Zum einen existiert eine große Anzahl bekannter, ionischer Hydrierkatalysatoren.^[74] Zum anderen scheint die Löslichkeit von Wasserstoff und vielen Alkenen in der ionischen Flüssigkeit ausreichend hoch zu sein, um gute Reaktionsgeschwindigkeiten zu erzielen. Gleichzeitig ist die Mischungslücke zwischen den gesättigten Reaktionsprodukten und der ionischen Flüssigkeit groß, sodass in den meisten Fällen eine zweiphasige Arbeitsweise möglich ist.

4.2. Oxidationen

Jüngste Arbeiten von Song und Roh belegen, dass die Verwendung von ionischen Flüssigkeiten auch in selektiven Oxidationen vorteilhaft sein kann.^[75] Sie untersuchten die Epoxidierung von z.B. 2,2-Dimethylchromen mit einem chiralen [Mn^{III}(salen)]-Katalysator ([*N,N'*-Bis(3,5-di-*tert*-butylsalicyliden)-1,2-cyclohexandiamin]mangan(III)-chlorid) in einer Mischung aus [BMIM]PF₆ und CH₂Cl₂ im Volumenverhältnis 1:4 [Gl. (12)]. Die Autoren beschreiben eine deutliche



Aktivierung des Katalysators durch die Zugabe der ionischen Flüssigkeit zum organischen Lösungsmittel. Der Umsatz der Epoxidierung von 2,2-Dimethylchromen lag beispielsweise nach zwei Stunden mit ionischer Flüssigkeit bei 86 %, während der gleiche Umsatz ohne ionische Flüssigkeit erst nach sechs Stunden erreicht werden konnte. In beiden Fällen wurde ein gleichbleibend hoher Enantiomerenüberschuss von 96 % erzielt.

Die Verwendung der ionischen Flüssigkeit eröffnete zudem eine einfache Möglichkeit zur Katalysatorrecycling, ohne dass der Katalysator dafür modifiziert werden muss. Nach Waschen der organischen Phase mit Wasser wurden die Produkte mit Hexan extrahiert und die zurückbleibende ionische Katalysatorlösung konnte wieder eingesetzt werden. Allerdings geht nach fünfmaligem Recyclieren der ionischen Katalysatorlösung der Umsatz von 83 auf 53 % zurück. Die Autoren begründen dies mit einer langsamen Zersetzung des eingesetzten [Mn^{III}(salen)]-Komplexes.

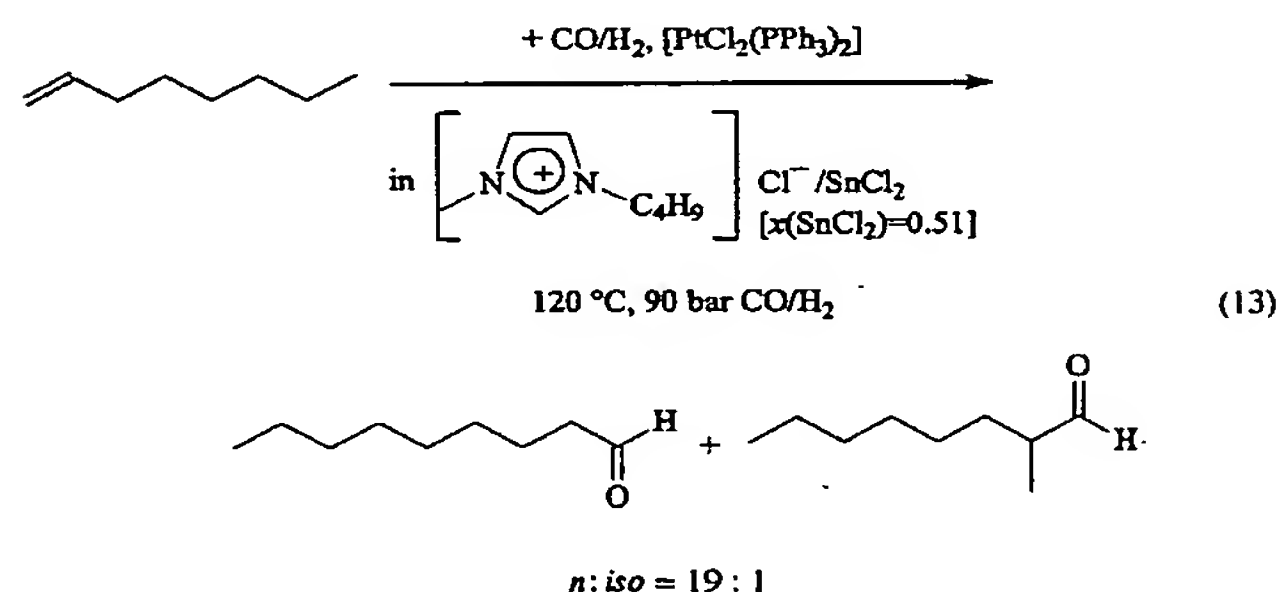
Unseres Wissens nach ist die Arbeit von Song und Roh die erste Veröffentlichung zur Übergangsmetall-katalysierten Oxidation unter Verwendung ionischer Flüssigkeiten. Dies ist insofern erstaunlich, als das Konzept der ionischen Flüssigkeiten gerade für Oxidationsreaktionen besonders

reizvoll erscheint. Aus elektrochemischen Untersuchungen weiß man, dass viele ionische Flüssigkeiten eine gute Oxidationsstabilität aufweisen.^[16a] Arbeiten aus unserer Gruppe zeigen zudem, dass beispielsweise niedrig schmelzende Pyridinium- oder Imidazoliumsalze mit Hydrogensulfat-Ionen selbst in stark oxidierenden Medien wie 30-proz. Oleum stabil sind, wenn kurzketige Alkylreste am Kation gewählt werden.^[76] Die Untersuchung weiterer Oxidationsreaktionen in ionischen Flüssigkeiten erscheint daher viel versprechend.

4.3. Hydroformylierungen

Bereits 1972 beschrieb Parshall die Platin-katalysierte Hydroformylierung von Ethen in Tetraethylammoniumtrichlorostannat-Schmelzen.^[31a] Das von ihm eingesetzte ionische Medium weist allerdings mit 78 °C einen recht hohen Schmelzpunkt auf. Außerdem wird in der Veröffentlichung nicht auf die katalytische Aktivität des in der Schmelze gelösten Platinkatalysators eingegangen.

In unserem Arbeitskreis haben wir daher die Platin-katalysierte Hydroformylierung in Chlorostannat-Schmelzen erneut aufgegriffen. In bei Raumtemperatur flüssigem BMIM-Trichlorostannat gelang die Hydroformylierung von 1-Octen gemäß Gleichung (13) mit bemerkenswerten *n*/*iso*-



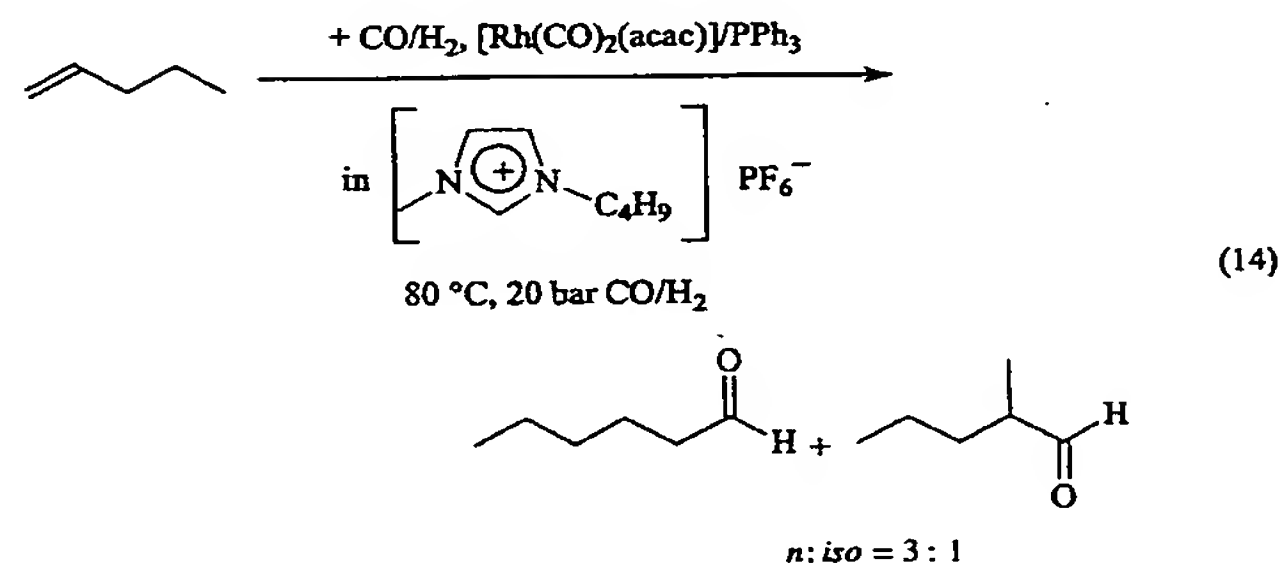
Selektivitäten.^[31c] Trotz der begrenzten Löslichkeit von 1-Octen in der ionischen Katalysatorphase konnte eine bemerkenswerte Aktivität des Platinkatalysators (Zahl der Mole Edukt, die pro Mol Katalysator und Stunde umgesetzt werden (turnover frequency, TOF): 126 h⁻¹) erreicht werden. Die Zweiphasigkeit der Reaktion erlaubt eine sehr einfache Produktabtrennung, ein Ausbluten des Platinkatalysators in die Produktphase wurde nicht beobachtet.

Die Ruthenium- und Cobalt-katalysierte Hydroformylierung von internen und endständigen Alkenen in geschmolzenem Tetra-*n*-butylphosphoniumbromid wurde von Knifton untersucht.^[23c] Der Autor beschreibt eine Stabilisierung des aktiven Rutheniumcarbonylkomplexes durch das ionische Medium. Diese macht sich in einer erhöhten Lebensdauer des Katalysators bei niedrigen Synthesegasdrücken und höheren Temperaturen bemerkbar.

In höher schmelzenden (> 70 °C) Phosphoniumsalzen wurde auch die Rhodium-katalysierte Hydroformylierung von 1-Hexen durchgeführt.^[24] Die Autoren nutzen den erhöhten Schmelzpunkt des Salzes, um das organische Produkt bei Raumtemperatur vom festen Katalysatormedium „abzue-

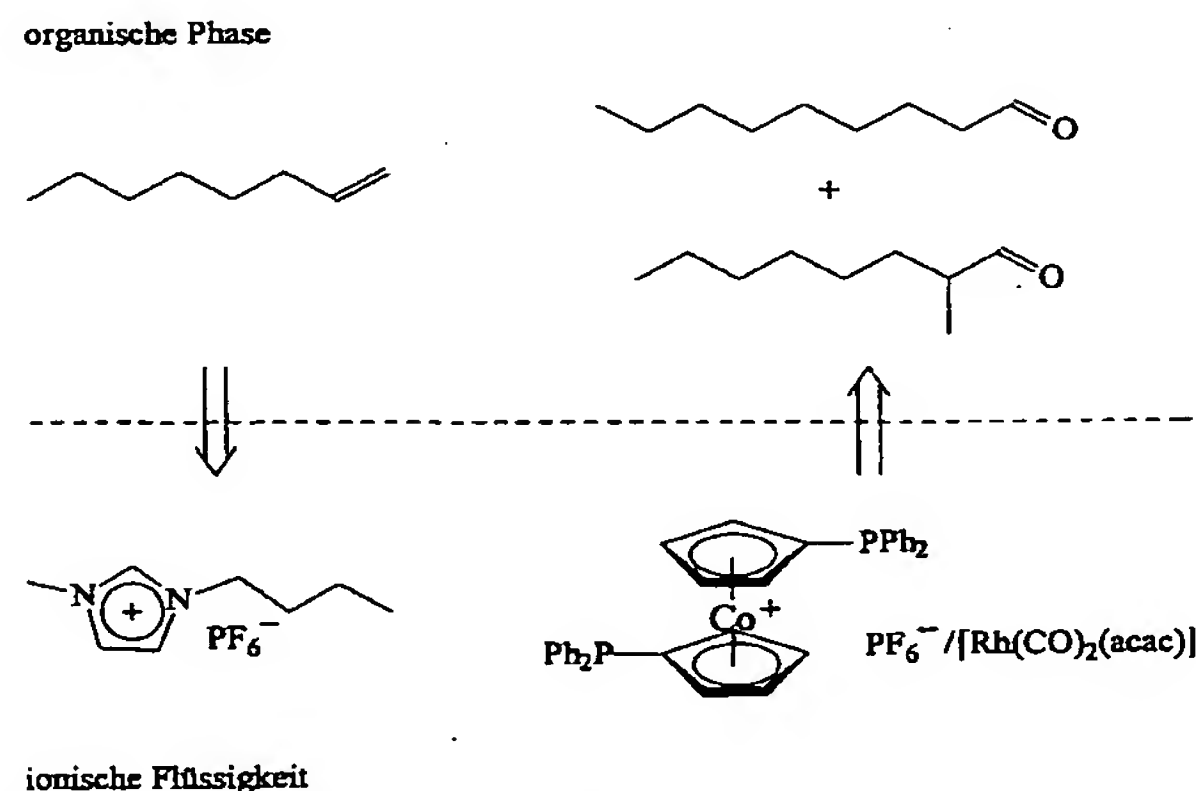
ben“. Nach erneutem Aufheizen über den Schmelzpunkt des Salzes kann das Katalysatorsystem erneut mit gleicher Reaktivität eingesetzt werden.

Arbeiten zur Rhodium-katalysierten Hydroformylierung in bei Raumtemperatur flüssigen Salzschnmelzen wurden 1995 von der Gruppe um Chauvin veröffentlicht.^[15, 77] Die Hydroformylierung von 1-Penten mit [Rh(CO)₂(acac)]/PPh₃ (acac = Acetylacetonat) gelang z.B. in einer [BMIM]PF₆-Schmelze [Gl. (14)]. Verglichen mit der Reaktion in Toluol



(TOF = 297 h⁻¹) konnte eine leicht verbesserte Aktivität (TOF = 333 h⁻¹) erzielt werden. Außerdem ermöglichte die zweiphasige Reaktionsführung eine einfache Produktabtrennung. Allerdings wurde bei dieser Reaktion ein leichtes Ausbluten des Katalysators in die organische Phase beobachtet. Durch den Einsatz von monosulfoiertem Triphenylphosphan (tppms) als Ligand konnte dies zwar vollständig unterdrückt werden, die Aktivität des Systems ging dabei jedoch deutlich zurück (TOF = 59 h⁻¹).

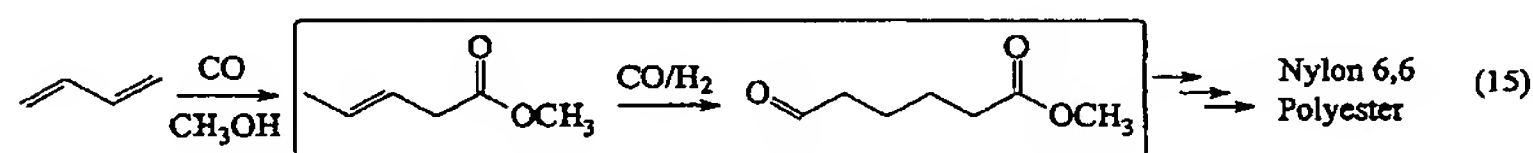
Das Ergebnis mit tppms wirft die Frage auf, ob die beobachtete Deaktivierung des Rh-Katalysators durch das ionische Reaktionsmedium oder durch den sulfonierten Liganden hervorgerufen wird. Wir haben daher in unserer Gruppe andere ionische Liganden zur Hydroformylierung in ionischen Flüssigkeiten getestet. Dabei erwiesen sich kationische Cobaltoceniumdiphosphan-Liganden in der zweiphasigen Hydroformylierung von 1-Octen in [BMIM]PF₆ als besonders erfolgreich (Schema 4).^[78] Die eingesetzten Cobaltoceniumdiphosphan-Liganden wurden vom Arbeitskreis



Schema 4. Zweiphasige, Rh-katalysierte Hydroformylierung von 1-Octen in [BMIM]PF₆ unter Verwendung eines kationischen Cobaltoceniumdiphosphanliganden.

Salzer entwickelt und zur Verfügung gestellt.^[79] Speziell mit dem Liganden 1,1'-Bis(diphenylphosphanyl)cobaltoceniumhexafluorophosphat konnten Aktivitäten erzielt werden ($\text{TOF} = 810 \text{ h}^{-1}$), die zumindest für eine zweiphasige Hydroformylierung von 1-Octen bemerkenswert sind. Auch die erzielte Selektivität zugunsten des linearen Aldehyds ($n:iso = 16.2:1$) ist in einem technisch interessanten Bereich. Der Katalysatorverlust in die organische Phase war kleiner als 0.5%, die prinzipielle Recyclierbarkeit des Katalysatorsystems konnte ebenfalls gezeigt werden. Offensichtlich ist in ionischen Flüssigkeiten die Rh-katalysierte, zweiphasige Hydroformylierung von langkettigen α -Olefinen mit hoher Aktivität und Selektivität möglich, wenn geeignete (kationische) Liganden eingesetzt werden.

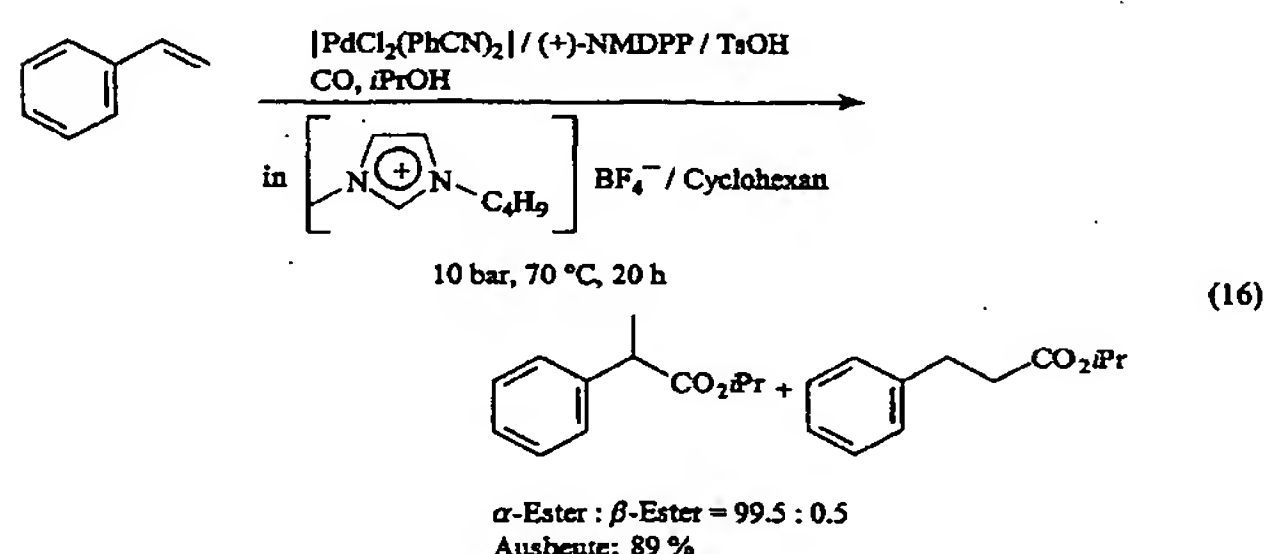
Interessanterweise ergeben sich nicht nur im Falle einer zweiphasigen Reaktionsführung verfahrenstechnische Vorteile bei der Hydroformylierung in ionischen Flüssigkeiten. Bei der einphasigen Hydroformylierung von Methyl-3-pentenoat gelang es durch Verwendung von [BMIM]PF₆ als Lösungsmittel, den Rhodiumkatalysator unter den harschen Bedingungen der Produktdestillation (0.2 mbar Vakuum, 110 °C) im Reaktor zu stabilisieren. Die ionische Katalysatorphase wurde zehnmal ohne Aktivitätsverlust recycelt.^[80] Die Gesamtproduktivität des eingesetzten Rh-Katalysators konnte auf diese Weise verzehnfacht werden. Die Reaktion ist als Schritt einer Synthese von Adipinsäure aus Butadien von technischer Bedeutung [Gl. (15)].



4.4. Alkoxy-carbonylierungen

Eine interessante, zweiphasige Variante der Palladium-katalysierten Alkoxy-carbonylierung von Styrol und Styrolderivaten wurde von Monteiro et al. veröffentlicht.^[18a] Im System BMIM-Tetrafluorborat/Cyclohexan wurden beispielsweise Styrol, Isopropanol und Kohlenmonoxid zu 2-Phenylpropionsäureisopropylester umgesetzt. Dabei konnte mit (+)-Neomenthyl-diphenylphosphan ((+)-NMDPP) als Ligand das Produkt in hoher Ausbeute und mit sehr guter Regioselektivität erhalten werden [Gl. (16)]. Trotz des chiralen Phosphanliganden war die beobachtete asymmetrische Induktion allerdings sehr gering ($ee < 5\%$).

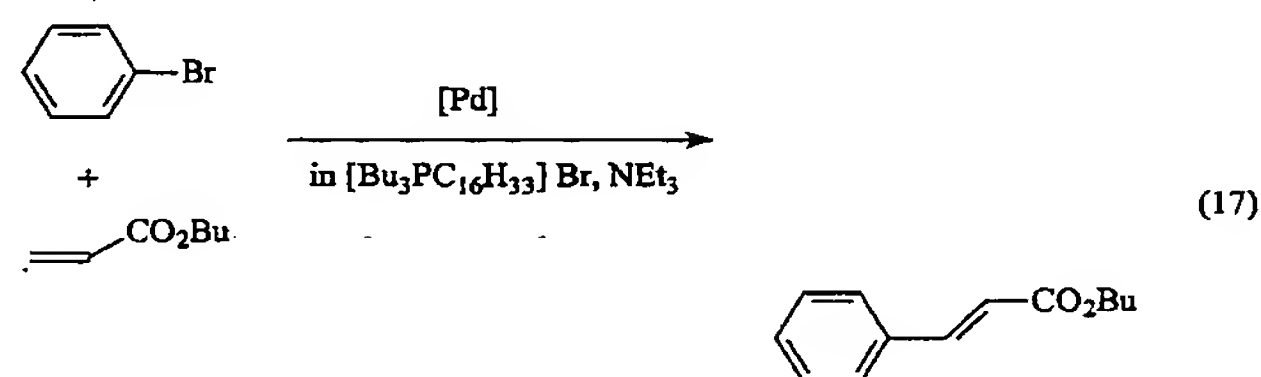
Die eingesetzte ionische Flüssigkeit erlaubt eine vereinfachte Produktisolierung durch die zweiphasige Reaktions-



führung. Eine Wiederverwendung der durch Phasentrennung zurückgewonnenen ionischen Katalysatorlösung gelingt jedoch nur, wenn zuvor der Umsatz der Reaktion auf $< 35\%$ beschränkt wird. Bei vollständigem Umsatz beobachten die Autoren dagegen die teilweise oder vollständige Zersetzung des aktiven Palladiumkatalysators.

4.5. Heck-Reaktionen

Die Verwendung ionischer Flüssigkeiten als Reaktionsmedium für die Palladium-katalysierte Heck-Reaktion wurde zuerst 1996 von der Gruppe um Kaufmann beschrieben.^[81] In geschmolzenem Tetraalkylammonium- und Tetraalkylphosphoniumbromid-Salzen gelang die Umsetzung von Brombenzol mit Acrylsäurebutylester zu *trans*-Zimtsäurebutylester in hohen Ausbeuten [Gl. (17)]. Die Autoren beschreiben einen stabilisierenden Effekt der ionischen Flüssigkeit auf den



Palladiumkatalysator. Selbst bei vollständigem Umsatz des Halogenarens wird in der Regel keine Ausfällung von elementarem Palladium beobachtet. Die Reaktionsprodukte konnten durch Destillation aus der ionischen Flüssigkeit isoliert werden.

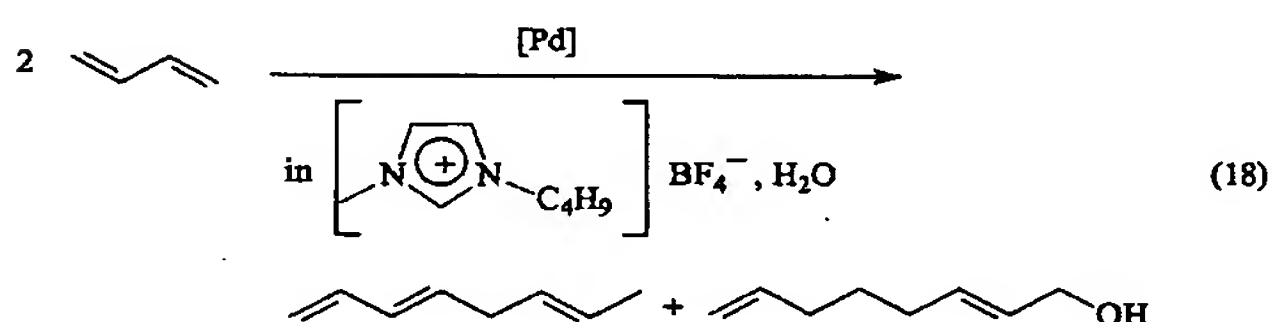
Umfassende Untersuchungen über Heck-Reaktionen in niedrig schmelzenden Salzen wurden jüngst von Herrmann und Böhm vorgestellt.^[82] Ihre Ergebnisse zeigen, dass ionische Flüssigkeiten speziell bei der Umsetzung der technisch interessanten Chlorarene deutliche Vorteile gegenüber molekularen, organischen Lösungsmitteln (wie DMF) aufweisen. Mit nahezu allen Katalysatorsystemen konnte eine zusätzliche Stabilisierung und Aktivierung erreicht werden. Unter den getesteten Systemen erwies sich dabei [NBu₄]Br (Schmelzpunkt 103 °C) als besonders geeignet. So konnte beispielsweise bei der Reaktion von Brombenzol mit Styrol unter Verwendung von Diiodobis(1,3-dimethylimidazolin-2-yliden)palladium(II) die Ausbeute an Stilben unter sonst identischen Bedingungen von 20 (DMF) auf über 99% ([NBu₄]Br) gesteigert werden. Auch hier wurden die Produkte von der nichtflüchtigen, ionischen Katalysatorlösung destillativ abgetrennt. Bis zu dreizehnmal konnte die ionische Katalysatorlösung ohne signifikante Aktivitätseinbußen recycelt werden. Als weitere Vorteile des neuartigen Lösungsmittelkonzepts werden die hervorragende Löslichkeit aller Reaktionspartner im ionischen Lösungsmittel sowie die Möglichkeit der Verwendung preiswerter anorganischer Basen genannt. Die Autoren urteilen zusammenfassend, dass sich die Verwendung von ionischen Flüssigkeiten in Zukunft als Standardverfahren zur Durchführung von Heck-Reaktionen etablieren könnte.

Weitere Varianten der Heck-Reaktion in ionischen Flüssigkeiten untersuchte die Gruppe um Seddon.^[83] Sie beschrieb die Möglichkeit einer dreiphasigen Aufarbeitung des Reaktionsgemisches im System [BMIM]PF₆/Wasser/Hexan. Während der verwendete Katalysator [(BMIM)₂PdCl₄] in der ionischen Flüssigkeit verbleibt, lösen sich die Produkte in der organischen Phase. Das während der Reaktion gebildeten Salz ([HBase]⁺X⁻) wird dagegen von der Wasserphase aufgenommen. Interessanterweise beobachteten die Autoren bei ihren Untersuchungen Reaktivitätsunterschiede, je nachdem, ob die in der Heck-Reaktion eingesetzten ionischen Flüssigkeiten Imidazolium- oder Pyridinium-Ionen enthielten. Sie vermuten in Imidazolium-Schmelzen eine Abstraktion des 2-H-Wasserstoffatoms durch die Hilfsbase der Heck-Reaktion und die Bildung von Palladiumcarbenkomplexen.

Die In-situ-Bildung von Palladiumcarbenkomplexen in Imidazolium-Schmelzen unter den Reaktionsbedingungen der Heck-Reaktion konnte vor kurzem die Gruppe um Xiao bestätigen.^[65] Sie berichten über eine deutlich höhere Aktivität der Heck-Reaktion in [BMIM]Br gegenüber der in [BMIM]BF₄ und erklärten dies mit der Tatsache, dass Palladiumcarbenkomplexe nur in der Bromid-Schmelze gebildet werden. Die entsprechenden Komplexe konnten aus der Bromid-Schmelze isoliert und charakterisiert werden. Die isolierten Komplexe konnten anschließend wieder als aktive Katalysatoren für die Heck-Reaktion in [BMIM]Br eingesetzt werden.

4.6. Hydrodimerisierungen/Telomerisationen

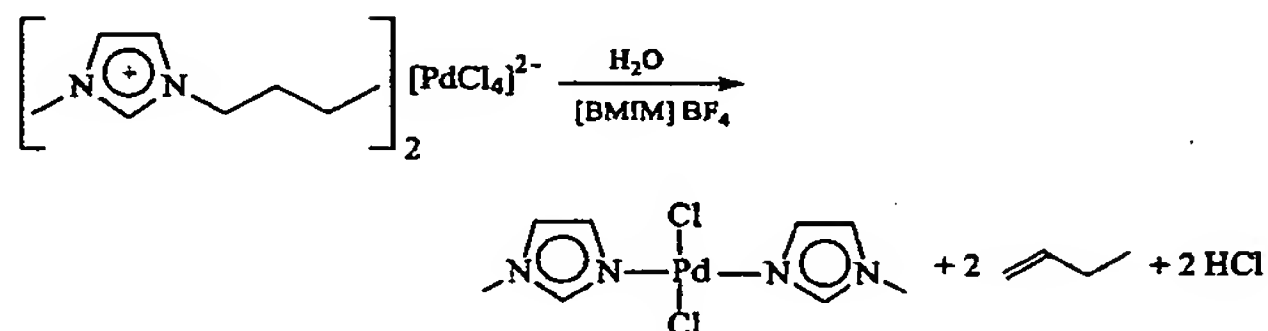
Die Gruppe um Dupont untersuchte die Hydrodimerisierung/Telomerisation von 1,3-Butadien mit Palladium(II)-Verbindungen in [BMIM]BF₄-Schmelzen.^[84] Dabei wird neben 1,3,6-Octatrien auch das Telomer Octa-2,7-dien-1-ol erhalten [Gl. (18)]. Die Aktivität des Katalysators wird mit TOF = 118 h⁻¹ angegeben und kann durch Arbeiten unter CO₂-Druck auf 204 h⁻¹ gesteigert werden. Interessanterweise



findet die Reaktion bei 70°C in einem einphasigen Reaktionssystem statt, beim Abkühlen auf 5°C bilden sich jedoch eine ionische Katalysatorphase und eine Produktphase. Auf diese Weise wird eine einfache Produktabtrennung möglich und die ionische Katalysatorphase kann wiedergewonnen werden.

Eine der eingesetzten Katalysatorvorstufen, der Komplex [(BMIM)₂PdCl₄], konnte röntgenspektroskopisch analysiert werden. Die Autoren beschreiben die Aktivierung dieses Komplexes über eine Palladium(IV)-Verbindung, die sich durch oxidative Addition des Imidazolium-Stickstoffatoms und der Alkylgruppe unter Bruch der C-N-Bindung des

[BMIM]-Ions bildet. Durch β -Eliminierung von 1-Buten und reduktive Eliminierung von HCl bildet sich der aktive Katalysatorkomplex Bis(methylimidazol)dichloropalladium (Schema 5). Die Reaktion findet allerdings nur in Gegenwart von Wasser statt.

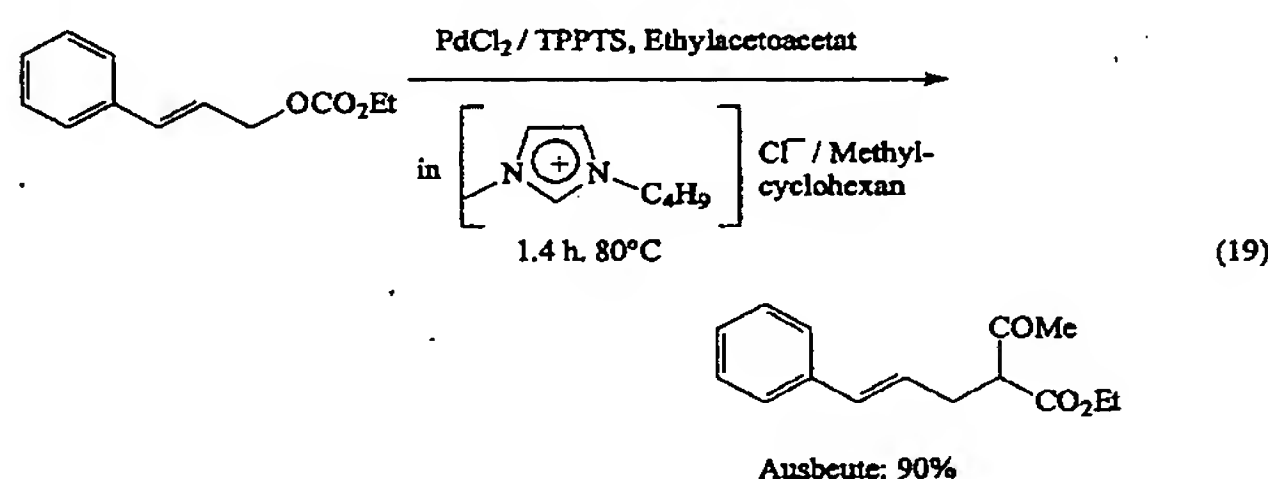


Schema 5. Bildung des aktiven Katalysators aus [(BMIM)₂PdCl₄] für die Hydrodimerisierung von 1,3-Butadien.

4.7. Trost-Tsuji-Kupplungen

Die Palladium(0)-katalysierte, nucleophile, allylische Substitution (Trost-Tsuji-Kupplung) ist ein attraktiver Weg zur Knüpfung von C-C-Bindungen in der organischen Synthese. Auch diese Reaktion konnte erfolgreich in ionischen Flüssigkeiten durchgeführt werden. Xiao et al. beschrieben die einphasige Umsetzung von 3-Acetoxy-1,3-diphenylprop-1-en mit Dimethylmalonat in BMIM-Tetrafluoroborat.^[85] Mit Pd(OAc)₂/PPh₃ (1/4) und K₂CO₃ als Base führte die Reaktion nach 5 h (80°C) zu vollständigem Umsatz. Das gewünschte Kupplungsprodukt konnte in 91 % Ausbeute isoliert werden. Als besonderer Vorteil der Verwendung einer ionischen Flüssigkeit wird die Möglichkeit genannt, das Nucleophil während der Reaktion in situ zu bilden.

Zweiphasige Varianten der Trost-Tsuji-Kupplung untersuchte die Gruppe um de Bellefon.^[86] Sie setzten Cinnamyl-ethylcarbonat mit Ethylacetoacetat im System [BMIM]Cl/Methylcyclohexan um und verglichen die Ergebnisse mit der Reaktion in Butyronitril/Wasser [Gl. (19)]. Offensichtlich



bietet die Verwendung des ionischen Katalysatormediums klare Vorteile gegenüber der Reaktion im wässrigen Zweiphasensystem. So wird eine Aktivitätssteigerung um den Faktor 10 beobachtet, die hauptsächlich auf eine deutlich bessere Löslichkeit der Edukte im ionischen Reaktionsmedium zurückgeführt werden kann. Ferner zeigt die Reaktion in [BMIM]Cl/Methylcyclohexan eine deutlich verbesserte Selektivität, da die Bildung von Zimtalkohol (durch Reaktion mit Wasser als Nucleophil) und die Bildung von Phosphoniumsalzen (durch Reaktion des Pd-Allylkomplexes mit trisulfoiertem Triphenylphosphan (tppts) als Ligand) in der ionischen Flüssigkeit ganz bzw. teilweise unterdrückt werden.

4.8. Oligomerisierungen

Viele kationische Übergangsmetallkomplexe sind als hochaktive Katalysatoren für Oligomerisierungen bekannt.^[87] Ihre Löslichkeit in unpolaren Lösungsmitteln ist jedoch häufig begrenzt, sodass man bei der Verwendung üblicher organischer Lösungsmittel gezwungen ist, einen Kompromiss zwischen den Solvatations- und den Koordinationseigenschaften des verwendeten Lösungsmittels einzugehen. Um eine ausreichende Katalysatorlöslichkeit zu erreichen, müssen häufig Lösungsmittel verwendet werden, die in gewisser Weise mit dem Substrat um die Koordinationsstellen am Katalysator konkurrieren. Einige ionische Flüssigkeiten – insbesondere Chloroaluminat-, Tetrafluoroborat- und Hexafluorophosphat-Schmelzen – eröffnen hier neue Perspektiven, da sie eine gewisse Polarität mit schwach koordinierenden Eigenschaften verbinden.

In unserem Arbeitskreis wurde z.B. die Ethenoligomerisierung mit dem Komplex $(\eta^3\text{-Methallyl})[\text{bis}(\text{diphenylphosphanyl})\text{methanmonoxid-}\kappa^2\text{P,O}]\text{nickel(II)-hexafluoroantimonat}$ $[(\eta^3\text{-methallyl})\text{Ni}(\text{dppmO})]\text{SbF}_6$ in verschiedenen Lösungsmitteln untersucht. Dabei erwies sich CH_2Cl_2 als das geeignetste organische Lösungsmittel.^[88] Durch die Verwendung von z.B. $[\text{BMIM}]\text{PF}_6$ konnte die Aktivität des kationischen Ni-Komplexes auf das rund siebenfache gesteigert werden.^[89] Die Gesamtselektivität der zweiphasigen Reaktion zugunsten linearer α -Olefine betrug über 88 % und lag damit sogar leicht über der der einphasigen Reaktion in CH_2Cl_2 .

In Tetrafluoroborat- und Hexafluorophosphat-Schmelzen wurde von der Gruppe um Dupont auch die Pd-katalysierte Dimerisierung von Butadien durchgeführt.^[18b] Die Verwendung des ionischen Lösungsmittels ermöglichte auch hier eine zweiphasige Reaktionsführung. Die Autoren beobachteten einen wesentlichen Aktivitätsanstieg des Katalysators im Vergleich zur Reaktion in Tetrahydrofuran.

Die Nickel-katalysierte Oligomerisierung kurzkettiger Alkene in Chloroaluminat-Schmelzen ist eine der am besten untersuchten Anwendungen von Übergangsmetallkatalysatoren in ionischen Flüssigkeiten.

Bereits 1990 veröffentlichte die Gruppe um Chauvin die ersten Untersuchungen zur Dimerisierung von Propen in ionischen Flüssigkeiten der Zusammensetzung $[\text{BMIM}]\text{Cl}/\text{AlCl}_3/\text{AlEtCl}_2$.^[12] Verwandte Systeme wurden in der Folge auch zur Oligomerisierung von Ethen^[90] und von Butenen^[91] eingesetzt.

Generell verdient die Nickel-katalysierte Dimerisierung in Chloroaluminat-Schmelzen besondere Beachtung, da ihre Kommerzialisierung unter dem Namen „Difasol-Prozess“ vom Institut Français du Pétrole (IFP) angekündigt worden

ist.^[36, 92] Eine erste industrielle Anwendung ionischer Flüssigkeiten ist damit in Aussicht gestellt worden.

Einige detailliertere Aspekte der Reaktion werden im Folgenden am Beispiel der Dimerisierung von Propen vorgestellt (Tabelle 9).^[12, 28a, 93] In basischen Schmelzen (Tabelle 9, Versuch a) erfolgt keine Dimerisierung. Vermutlich verhindert das basische Chlorid-Ion die Bildung freier Koordinationsstellen am Nickelkatalysator. In aciden Chloroaluminat-Schmelzen findet dagegen selbst ohne einen Nickelkatalysator eine Oligomerisierung statt (Tabelle 9, Versuch b). Allerdings werden dabei nicht die gewünschten Dimere, sondern ein Gemisch unterschiedlichster Oligomere erhalten, die durch kationische Aufbaureaktionen gebildet werden. Als Ursache werden superacide Protonen und die Reaktivität der aciden Anionen Al_2Cl_7^- und $\text{Al}_3\text{Cl}_{10}^-$ vermutet.^[12, 60] Durch Zugabe von Aluminiumalkylverbindungen lässt sich diese unerwünschte kationische Oligomerisierung vollständig unterdrücken. In Gegenwart von NiCl_2 als Katalysatorvorstufe weist die gebildete ionische Katalysatorlösung eine gute Aktivität in der Dimerisierung von Propen auf (Tabelle 9, Versuch c). Ohne zusätzlichen Phosphanliganden ergibt sich dabei eine Produktverteilung, die keine besondere Selektivität zugunsten der begehrten, hochverzweigten Produkte erkennen lässt. Mit zugesetztem Phosphanliganden ist die Produktverteilung vom sterischen Anspruch des eingesetzten Liganden abhängig (Tabelle 9, Versuch d). Dies entspricht den Ergebnissen früherer Arbeiten von Wilke und Bogdanović in organischen Lösungsmitteln.^[94] Es werden Selektivitäten zugunsten des begehrten, hochverzweigten Dimers, des 2,3-Dimethylbutens, von bis zu 83 % erreicht. Bei längerer Versuchsdauer wird allerdings eine Abnahme der Selektivität zu hochverzweigten Produkten beobachtet. Es wird eine Konkurrenzreaktion des basischen Phosphanliganden mit der harten Lewis-Säure AlCl_3 vermutet [Gl. (20)]. Diese Annahme wird dadurch gestützt, dass durch die Zugabe einer weichen Konkurrenzbase wie Tetramethylbenzol die Selektivitätsverluste vermieden werden können.



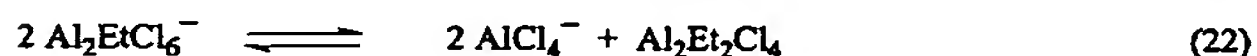
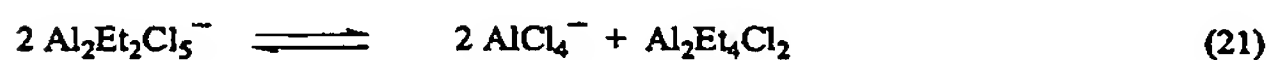
Leider gelten beim Arbeiten mit ionischen Flüssigkeiten, die große Anteile an AlEtCl_2 enthalten, gewisse Einschränkungen: Die Reduktionswirkung der Aluminiumalkylverbindungen begrenzt die Temperaturstabilität des Nickelkatalysators: Bei sehr hohen Aluminiumalkylkonzentrationen fällt bereits bei Raumtemperatur nach kurzer Zeit schwarzes, metallisches Nickel aus. Außerdem werden bei längerer Versuchsdauer geringe Anteile der Aluminiumalkylverbin-

Tabelle 9. Ergebnisse der Propen-Dimerisierung in ionischen Flüssigkeiten bei -15°C .

Nr.	ionische Flüssigkeit	Zusammensetzung	Ni-Komplex	Aktivität [kg (g(Ni)) ⁻¹ h ⁻¹]	Produktverhältnis DMB:M2P:nHex ^[a]
a)	$[\text{BMIM}]\text{Cl}/\text{AlCl}_3$	1/0.8	$[\text{NiBr}_2\text{L}_2]^{\text{[b]}}$	0	
b)	$[\text{BMIM}]\text{Cl}/\text{AlCl}_3$	1/1.5	–	– ^[c]	
c)	$[\text{BMIM}]\text{Cl}/\text{AlEtCl}_2$	1/1.2	NiCl_2	2.5	5:74:21
d)	$[\text{BMIM}]\text{Cl}/\text{AlEtCl}_2$	1/1.2	$[\text{NiCl}_2(\text{iPr}_3\text{P})_2]$	2.5	74:24:2
e)	$[\text{BMIM}]\text{Cl}/\text{AlCl}_3/\text{AlEtCl}_2$	1/1.2/0.1	$[\text{NiCl}_2(\text{iPr}_3\text{P})_2]$	12.5	83:15:2

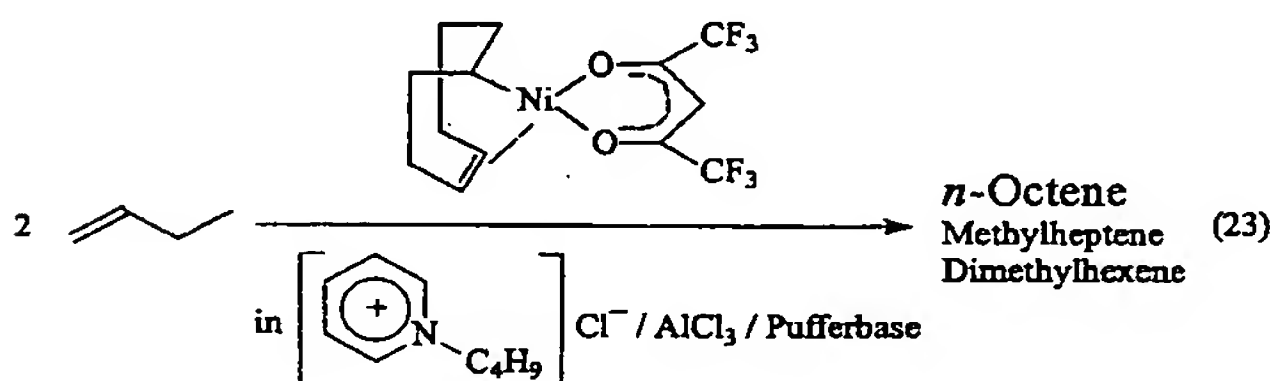
[a] DMB = Dimethylbuten, M2P = Methylpenten, nHex = n-Hexen. [b] L = 2-Methylallyl. [c] Es wurden hochviskose kationische Oligomere erhalten.

dung in die organische Phase ausgewaschen. Dies verändert die Zusammensetzung und die chemischen Eigenschaften des ionischen Lösungsmittels. An der Phasengrenzschicht werden die Gleichgewichte (21) und (22) angenommen.^[28]



Dennoch besitzt das vom IFP entwickelte, zweiphasige Difasol-Verfahren, das Chloroaluminat-Schmelzen mit geringen Anteilen an Aluminiumalkylverbindungen als Katalysatorphase nutzt, erhebliche Vorteile gegenüber dem einphasigen, technisch realisierten Dimersol-Verfahren (derzeit sind 25 Anlagen mit einer Kapazität von 3.4 Millionen Tonnen pro Jahr in Betrieb^[92b]). Laut IFP kann der Nickelverbrauch und der Verbrauch an Aluminiumalkylverbindungen deutlich herabgesetzt werden. Weitere Vorteile bestehen in der guten Toleranz gegenüber stark verdünnten Gemischen und in der deutlich höheren Selektivität des zweiphasigen Verfahrens zugunsten des Dimers.^[92]

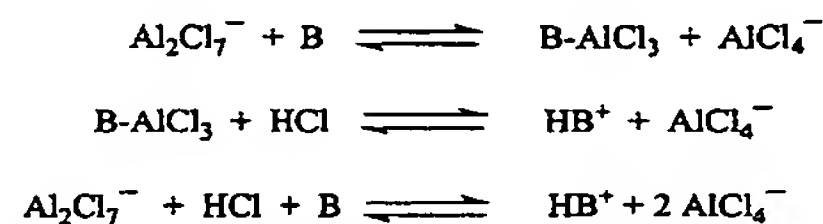
In unserer Arbeitsgruppe haben wir die Eignung von Chloroaluminat-Schmelzen für die Lineardimerisierung von 1-Buten mit dem Nickelkatalysator (η -4-Cycloocten-1-yl)-(1,1,1,5,5,5-hexafluor-2,4-pentandionato-*O,O'*)nickel [(Hcod)-Ni(hfacac)] (Hcod = Cyclooct-4-en-1-yl) gemäß Gleichung (23) untersucht. Dabei erwiesen sich Systeme, die Aluminiumalkylverbindungen enthalten, als ungeeignet, da sie zu einer starken Isomerisierung des eingesetzten 1-Butens führen.^[91] Da nur das α -Olefin zu linearen Octenen verknüpft werden kann, behindert eine Isomerisierungsaktivität des Lösungsmittels die Bildung der gewünschten Produkte.



Wir haben daher Chloroaluminat-Schmelzen entwickelt, die auch ohne die Zugabe von Aluminiumalkylverbindungen eine selektive, Nickel-katalysierte C-C-Verknüpfung in ionischen Flüssigkeiten ermöglichen.^[60, 95] Bei Zugabe schwacher organischer Basen, wie etwa Chinolin oder Pyrrol, zu einer

aciden Chloroaluminat-Schmelze wird ein Reaktionsmedium erhalten, in dem der Katalysator bei nur geringfügig geringerer Selektivität zugunsten des linearen Produkts deutlich aktiver ist als in Toluol (Tabelle 10).

Die Funktion der zugegebenen Base besteht darin, alle aciden Spezies in der ionischen Flüssigkeit abzupuffern, die unselektive, kationische Aufbaureaktionen katalysieren könnten (Schema 6).



Schema 6. Unterdrückung kationischer Nebenreaktionen in aciden Chloroaluminat-Schmelzen durch Zugabe einer schwachen organischen Base B.

Neben der Aktivierung des Katalysators [(Hcod)Ni(hfacac)] in der ionischen Flüssigkeit interessierten uns vor allem Aspekte der Lebensdauer und der Gesamtaktivität des ionischen Katalysatorsystems. Zu diesem Zweck wurde ein kontinuierlich arbeitender Schlaufenreaktor aufgebaut (Abbildung 8).^[96] Die ionische Katalysatorlösung wird bei Reaktionsbeginn vorgelegt und die Schlaufe mit Edukt gefüllt. Während des Versuches wird das Edukt kontinuierlich nachgeführt. Über den integrierten Abscheider innerhalb der Reaktorschlaufe wird die Trennung von ionischer Katalysatorlösung und organischer Produktphase vorgenommen. Da sich die ionische Katalysatorlösung zu jedem Zeitpunkt vollständig in der Reaktorschlaufe befindet, können alle Veränderungen des Systems anhand der aufgefangenen Produkte ohne zeitliche Verzögerung registriert werden. Kontinuierliche Versuche zur Lineardimerisierung von 1-Buten ergaben eine Gesamtaktivität (turnover number, TON) des Katalysators [(Hcod)Ni(hfacac)] von über 18000.^[97]

5. Zusammenfassung und Ausblick

Ionische Flüssigkeiten stellen eine einzigartige Klasse neuer Reaktionsmedien für die Übergangsmetallkatalyse dar. Bereits ihre nichtflüchtige Natur bringt erhebliche verfahrenstechnische Vorteile bei der destillativen Produktabtrennung aus ionischen Reaktionslösungen und unterbindet zudem einen Lösungsmittelverlust durch unkontrolliertes Abdampfen. Die Möglichkeit der gezielten Variation ihrer physikalischen und chemischen Eigenschaften macht ionische

Tabelle 10. Vergleich der Lineardimerisierung von 1-Buten mit [(Hcod)Ni(hfacac)] in Toluol und in Chloroaluminat-Schmelzen.

Reaktion in Toluol	Reaktion in [4-MBP]Cl/AlCl ₃ /Chinolin (0.43/0.53/0.04) ^[a]
<ul style="list-style-type: none"> • einphasig • keine Aktivität des Katalysators bei < 50 °C • Ergebnisse bei 90 °C:^[b] TOF = 500 h⁻¹ Dimerselektivität 85 % Linearselektivität 75 % 	<ul style="list-style-type: none"> • zweiphasig, kein nachweisbares Ausbluten des Katalysators • deutliche Aktivität selbst bei -10 °C • Ergebnisse bei 25 °C:^[b] TOF = 1240 h⁻¹ Dimerselektivität 98 % Linearselektivität 64 %

[a] 4-MBP = 1-*n*-Butyl-4-methylpyridinium-Ion. [b] Bei 20 % Umsatz.

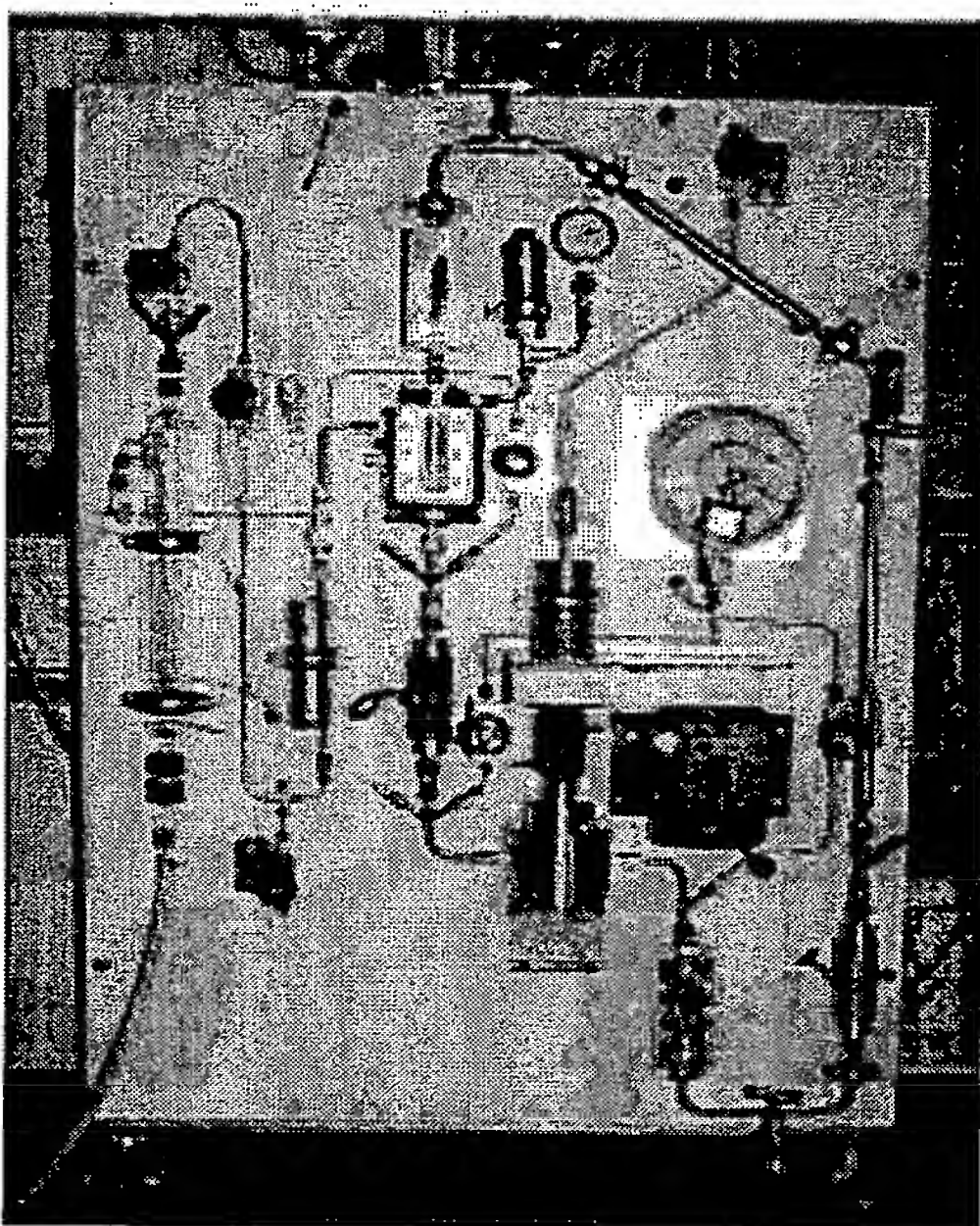
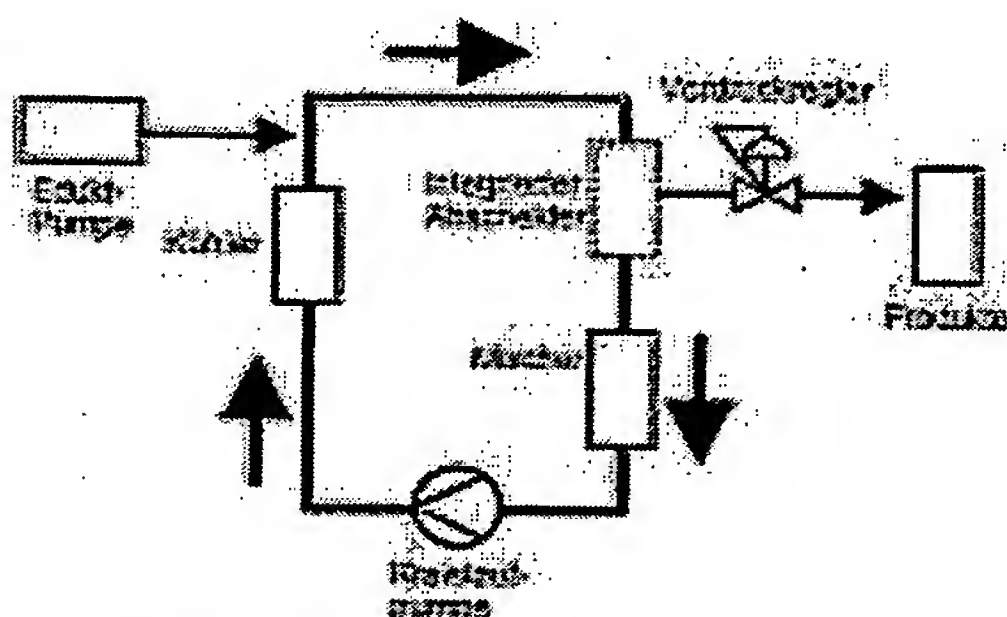


Abbildung 8. Schematische Darstellung und Ansicht eines Schlaufenreaktors zur Ermittlung der Lebensdauer ionischer Übergangsmetallkatalysator-Lösungen.

Flüssigkeiten zu idealen Kandidaten für Anwendungen in der Zweiphasenkatalyse.

Die genannten Vorteile lassen sich in vielen Anwendungen nutzen, um den Lösungsmittel- oder Katalysatorverbrauch zu minimieren. Daher werden ionische Flüssigkeiten mit Recht als „Green Solvents“ diskutiert.^[36, 68] Ionische Flüssigkeiten ergänzen dabei in sehr attraktiver Weise andere Green-Solvent-Konzepte, wie z.B. die Verwendung von überkritischem CO₂ oder Wasser. Während überkritisches CO₂ den Bereich der Anwendungen mit unpolaren Lösungsmitteln abdeckt, kommen ionische Flüssigkeiten zur Substitution polarer organischer Lösungsmittel in Betracht. Erste Arbeiten zur erfolgreichen Kombination beider Lösungsmittelkonzepte wurden bereits veröffentlicht.^[49]

Im Unterschied zu Wasser sind ionische Flüssigkeiten sicher auch langfristig wesentlich teurer und werden daher vor allem dort Anwendung finden, wo wässrige Reaktionssysteme ungeeignet sind oder zu großen Problemen führen. In diesem Zusammenhang ist die oft unerwünschte Reaktivität von Wasser gegenüber aktiven Katalysatoren als limitieren-

der Faktor zu nennen. Außerdem ist die Löslichkeit vieler Edukte in Wasser begrenzt.

In zahlreichen Anwendungen sind ionische Flüssigkeiten mit schwach koordinierenden, inerten Anionen und geeignet substituierten Kationen eine attraktive Alternative zu den herkömmlich verwendeten Lösungsmitteln. Dabei führt der Wechsel von einem organischen Lösungsmittel zu einem ionischen Reaktionsmedium häufig auch zu einer veränderten chemischen Reaktivität der gelösten Spezies. Die vorgestellten Beispiele zeigen, dass bekannte Reaktionen in geeigneten ionischen Flüssigkeiten in vielen Fällen beschleunigt und mit veränderter Selektivität ablaufen. In einigen Fällen wird auch eine erhöhte Stabilität der untersuchten Katalysatorsysteme in ionischen Flüssigkeiten beobachtet.

Darüber hinaus scheinen die ungewöhnlichen Eigenschaften ionischer Flüssigkeiten ein enormes Innovationspotential für die Übergangsmetallkatalyse zu erschließen. Beispielsweise ist die Bildung von Flüssigkristallphasen in bestimmten ionischen Flüssigkeiten bekannt^[1, 17a,d] und vor kurzem wurde über Hinweise auf eine geordnete Struktur an der Oberfläche von ionischen Flüssigkeiten berichtet.^[98] Ergeben sich hier neue Ansätze zur Untersuchung von Übergangsmetallkatalysatoren in hochgeordneten Lösungsmitteln? Oder gelingt es, die elektrochemischen Eigenschaften ionischer Flüssigkeiten zu nutzen, um Übergangsmetallkatalysatoren in bestimmten, vielleicht ungewöhnlichen Oxidationszuständen aktiv zu halten? Die Verwendung ionischer Flüssigkeiten als Lösungsmittel in der Übergangsmetallkatalyse öffnet ein weites Feld für zukünftige Untersuchungen.

Die in diesem Beitrag erwähnten Arbeiten aus unserer Gruppe wurden von BP-Amoco Chemicals, von der Europäischen Gemeinschaft im Rahmen des BRITE-Projekts 96-3745, von der Max-Buchner-Stiftung sowie vom Ministerium für Schule und Weiterbildung, Wissenschaft und Forschung des Landes Nordrhein-Westfalen im Rahmen des Katalyseverbundes Nordrhein-Westfalen unterstützt. Die Autoren danken Dr. M. Eichmann, Dr. H. Waffenschmidt, M. Sasing und H. Wolff für ihre Beiträge zu diesem Manuskript. Unser Dank gilt ferner Prof. K. R. Seddon für zahlreiche Anregungen, die vor allem zu Beginn unserer Beschäftigung mit ionischen Flüssigkeiten sehr hilfreich waren.

Eingegangen am 15. März 1999 [A 333]

- [1] a) K. R. Seddon, *J. Chem. Tech. Biotechnol.* **1997**, *68*, 351–356; b) K. R. Seddon, *Kinet. Catal. Engl. Transl.* **1996**, *37*, 693–697.
- [2] a) W. Sundermeyer, *Angew. Chem.* **1965**, *77*, 241–258; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 222–239; b) W. Sundermeyer, *Chem. Unserer Zeit* **1967**, *1*, 150–157; c) S. V. Volkov, *Chem. Soc. Rev.* **1990**, *19*, 21–28.
- [3] S. Sugden, H. Wilkins, *J. Chem. Soc.* **1929**, 1291–1298, zit. Lit.
- [4] I.-M. Herford, H. Schneider, *Liebigs Ann. Chem.* **1991**, 27–31.
- [5] a) F. H. Hurley, U.S. Patent 2,446,331, **1948** [*Chem. Abstr.* **1949**, *43*, P7645b]; b) F. H. Hurley, T. P. Wier, Jr., *J. Electrochem. Soc.* **1951**, *98*, 207–212.
- [6] a) H. L. Chum, V. R. Koch, L. L. Miller, R. A. Osteryoung, *J. Am. Chem. Soc.* **1975**, *97*, 3264–3265; b) J. Robinson, R. A. Osteryoung, *J. Am. Chem. Soc.* **1979**, *101*, 323–327; c) J. S. Wilkes, J. A. Levinsky, R. A. Wilson, C. L. Hussey, *Inorg. Chem.* **1982**, *21*, 1263–1264.

- [7] C. G. Swain, A. Ohno, D. K. Roe, R. Brown, T. Maugh II, *J. Am. Chem. Soc.* **1967**, *89*, 2648–2649.
- [8] a) T. B. Scheffler, C. L. Hussey, K. R. Seddon, C. M. Kear, P. D. Armitage, *Inorg. Chem.* **1983**, *22*, 2099–2100; b) T. M. Laher, C. L. Hussey, *Inorg. Chem.* **1983**, *22*, 3247–3251; c) T. B. Scheffler, C. L. Hussey, *Inorg. Chem.* **1984**, *23*, 1926–1932; d) P. B. Hitchcock, T. J. Mohammed, K. R. Seddon, J. A. Zora, C. L. Hussey, E. H. Ward, *Inorg. Chim. Acta* **1986**, *113*, L25–L26.
- [9] a) D. Appleby, C. L. Hussey, K. R. Seddon, J. E. Turp, *Nature* **1986**, *323*, 614–616; b) A. J. Dent, K. R. Seddon, T. Welton, *J. Chem. Soc. Chem. Commun.* **1990**, 315–316.
- [10] J. A. Boon, J. A. Levisky, J. L. Pflug, J. S. Wilkes, *J. Org. Chem.* **1986**, *51*, 480–483.
- [11] S. E. Fry, N. J. Pienta, *J. Am. Chem. Soc.* **1985**, *107*, 6399–6400.
- [12] Y. Chauvin, B. Gilbert, I. Guibard, *J. Chem. Soc. Chem. Commun.* **1990**, 1715–1716.
- [13] R. T. Carlin, R. A. Osteryoung, *J. Mol. Catal.* **1990**, *63*, 125–129.
- [14] J. S. Wilkes, M. J. Zaworotko, *J. Chem. Soc. Chem. Commun.* **1992**, 965–967.
- [15] Y. Chauvin, L. Musmann, H. Olivier, *Angew. Chem.* **1995**, *107*, 2941–2943; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2698–2700.
- [16] a) P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, *35*, 1168–1178; b) J. H. Davis, Jr., K. J. Forrester, *Tetrahedron Lett.* **1999**, *40*, 1621–1622; c) J. H. Davis, Jr., K. J. Forrester, T. Merrigan, *Tetrahedron Lett.* **1998**, *39*, 8955–8958; d) R. Hagiwara, T. Hirashige, T. Tsuda, Y. Ito, *J. Fluorine Chem.* **1999**, *99*, 1–3; e) M. Hasan, I. V. Kozhevnikov, M. R. H. Siddiqui, A. Steiner, N. Winterton, *Inorg. Chem.* **1999**, *38*, 5637–5641; f) W. Keim, W. Korth, P. Wasserscheid, WO 2000016902, 2000 [*Chem. Abstr.* **2000**, *132*, P238691].
- [17] a) C. M. Gordon, J. D. Holbrey, A. R. Kennedy, K. R. Seddon, *J. Mater. Chem.* **1998**, *8*, 2627–2636; b) P. A. Z. Suarez, S. Einloft, J. E. L. Dullius, R. F. de Souza, J. Dupont, *J. Chim. Phys.* **1998**, *95*, 1626–1639; c) A. J. Carmichael, C. Hardacre, J. D. Holbrey, M. Nieuwenhuyzen, K. R. Seddon, *Anal. Chem.* **1999**, *71*, 4572–4574; d) J. D. Holbrey, K. R. Seddon, *J. Chem. Soc. Dalton Trans.* **1999**, 2133–2140.
- [18] a) D. Zim, R. F. de Souza, J. Dupont, A. L. Monteiro, *Tetrahedron Lett.* **1998**, *39*, 7071–7074; b) S. M. Silva, P. A. Z. Suarez, R. F. de Souza, J. Dupont, *Polymer Bull.* **1998**, *40*, 401–405; c) P. J. Dyson, D. J. Ellis, D. G. Parker, T. Welton, *Chem. Commun.* **1999**, 25–26; d) C. M. Gordon, A. McCluskey, *Chem. Comm.* **1999**, 1431–1432; e) M. J. Earle, P. B. McCormac, K. R. Seddon, *Green Chemistry* **1999**, *1*, 23–25; f) C. W. Lee, *Tetrahedron Lett.* **1999**, *40*, 2461–2464; g) D. Crofts, P. J. Dyson, K. M. Sanderson, N. Srinivasan, T. Welton, *J. Organomet. Chem.* **1999**, *573*, 292–298; h) T. Fischer, A. Sethi, T. Welton, J. Woolf, *Tetrahedron Lett.* **1999**, *40*, 793–796; i) R. Y. Saleh, WO 2000015594, 2000 [*Chem. Abstr.* **2000**, *132*, P222341]; j) C. J. Adams, M. J. Earle, K. R. Seddon, *Green Chemistry* **2000**, *2*, 21–23; k) L. Green, I. Hemeon, R. D. Singer, *Tetrahedron Lett.* **2000**, *41*, 1343–1346.
- [19] T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2083.
- [20] J. D. Holbrey, K. R. Seddon, *Clean Products and Processes* **1999**, *1*, 223–226.
- [21] R. L. Hussey in *Chemistry of Nonaqueous Solutions* (Hrsg.: G. Mamantov, A. I. Popov), VCH, Weinheim, **1994**, S. 227–276.
- [22] a) R. T. Carlin, J. S. Wilkes in *Chemistry of Nonaqueous Solutions* (Hrsg.: G. Mamantov, A. I. Popov), VCH, Weinheim, **1994**, S. 277–306; b) C. L. Hussey, *Pure Appl. Chem.* **1988**, *60*, 1763–1772.
- [23] a) Imidazoliumsalze mit längeren Alkylketten: A. A. K. Abdul-Sada, P. W. Ambler, P. K. G. Hodgson, K. R. Seddon, N. J. Steward, WO 95/21871, **1995** [*Chem. Abstr.* **1995**, *123*, P341298k]; b) Ammoniumsalze: R. H. Dubois, M. J. Zaworotko, P. S. White, *Inorg. Chem.* **1989**, *28*, 2019–2020; c) Phosphoniumsalze: J. F. Knifton, *J. Mol. Catal.* **1987**, *43*, 65–78; d) Trialkylammoniumsalze: C. P. M. Lacroix, F. H. M. Dekker, A. G. Talma, J. W. F. Seetz, EP 989134, **1998** [*Chem. Abstr.* **2000**, *132*, 237092].
- [24] N. Karodia, S. Guise, C. Newlands, J.-A. Andersen, *Chem. Commun.* **1998**, 2341–2342.
- [25] H. Waffenschmidt, Dissertation, RWTH Aachen, **2000**.
- [26] H. A. Øye, M. Jagtoyen, T. Oksefjell, J. S. Wilkes, *Mater. Sci. Forum* **1991**, *73–75*, 183–189.
- [27] a) Z. J. Karpinski, R. A. Osteryoung, *Inorg. Chem.* **1984**, *23*, 1491–1494; b) A. A. K. Abdul-Sada, A. M. Greenway, K. R. Seddon, T. Welton, *Org. Mass Spectrom.* **1993**, *28*, 759–765.
- [28] a) Y. Chauvin, S. Einloft, H. Olivier, *Ind. Eng. Chem. Res.* **1995**, *34*, 1149–1155; b) B. Gilbert, Y. Chauvin, H. Olivier, F. Di Marco-Van Tiggelen, *J. Chem. Soc. Dalton Trans.* **1995**, 3867–3871.
- [29] S. D. Williams, J. P. Schoebrechts, J. C. Selkirk, G. Mamantov, *J. Am. Chem. Soc.* **1987**, *109*, 2218–2219.
- [30] Y. Chauvin, H. Olivier-Bourbigou, *CHEMTECH* **1995**, *25*, 26–30.
- [31] a) G. W. Parshall, *J. Am. Chem. Soc.* **1972**, *94*, 8716–8719; b) G. Ling, N. Koura, *Denki Kagaku oyobi Kogyo Butsuri Kagaku* **1997**, *65*, 149–153; c) H. Waffenschmidt, P. Wasserscheid, *J. Mol. Catal.*, im Druck.
- [32] P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza, J. Dupont, *Polyhedron*, **1996**, *15*, 1217–1219.
- [33] J. Fuller, R. T. Carlin, H. C. de Long, D. Haworth, *J. Chem. Soc. Chem. Commun.* **1994**, 299–300.
- [34] W. T. Ford, R. J. Hauri, D. J. Hart, *J. Org. Chem.* **1973**, *38*, 3916–3918.
- [35] S. P. Zingg, A. S. Dworkin, M. Sorlie, D. M. Chapman, A. C. Buchanan, G. P. Smith, *J. Electrochem. Soc.* **1984**, *131*, 1602–1608.
- [36] M. Freemantle, *Chem. Eng. News* **1998**, *76*, 32–37.
- [37] *CRC Handbook of Chemistry and Physics*, 73. Aufl. (Hrsg.: D. R. Lide), CRC Press, Boca Raton, **1992**.
- [38] A. Elaiwi, P. B. Hitchcock, K. R. Seddon, N. Srinivasan, Y.-M. Tan, T. Welton, J. A. Zora, *J. Chem. Soc. Dalton Trans.* **1995**, 3467–3472.
- [39] H. Stegemann, A. Rhode, A. Reiche, A. Schnitke, H. Füllbier, *Electrochim. Acta* **1992**, *37*, 379–383.
- [40] A. A. Fannin, Jr., D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes, J. L. Williams, *J. Phys. Chem.* **1984**, *88*, 2614–2621.
- [41] M. L. Mutch, J. S. Wilkes, *Proc. Electrochem. Soc.* **1998**, *98*, 254–260.
- [42] J. R. Sanders, E. H. Ward, C. L. Hussey, *J. Electrochem. Soc.* **1986**, *133*, 325–330.
- [43] S. Tait, R. A. Osteryoung, *Inorg. Chem.* **1984**, *23*, 4352–4360.
- [44] C. J. Dymek, D. A. Grob, A. V. Fratini, W. W. Adams, *J. Mol. Struct.* **1989**, *213*, 25–34.
- [45] R. A. Mantz, P. C. Trulove, R. T. Carlin, R. A. Osteryoung, *Inorg. Chem.* **1995**, *34*, 3846–3847.
- [46] J. Fuller, R. T. Carlin, R. A. Osteryoung, *J. Electrochem. Soc.* **1997**, *144*, 3881–3886.
- [47] a) R. L. Perry, K. M. Jones, W. D. Scott, Q. Liao, C. L. Hussey, *J. Chem. Eng. Data* **1995**, *40*, 615–619; b) Q. Liao, C. L. Hussey, *J. Chem. Eng. Data* **1996**, *41*, 1126–1130; c) P. Wasserscheid, Dissertation, RWTH Aachen, **1998**.
- [48] a) J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, R. D. Rogers, *Chem. Commun.* **1998**, 1765–1766; b) A. E. Visser, R. P. Swatloski, R. D. Rogers, *Green Chemistry* **2000**, *2*, 1–4.
- [49] L. A. Blanchard, D. Hancu, E. J. Beckman, J. F. Brennecke, *Nature* **1999**, *399*, 28–29.
- [50] C. Reichardt, *Nachr. Chem. Tech. Lab.* **1997**, *45*, 759–763.
- [51] K. Dimroth, C. Reichardt, T. Siepmann, F. Bohlmann, *Liebigs Ann. Chem.* **1963**, *661*, 1–37.
- [52] C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319–2358.
- [53] C. Reichardt, E. Harbusch-Görnert, *Liebigs Ann. Chem.* **1983**, *721*–743.
- [54] S. K. Poole, P. H. Shetty, C. F. Poole, *Anal. Chim. Acta* **1989**, *218*, 241–263.
- [55] C. Gordon, persönliche Mitteilung.
- [56] D. W. Armstrong, L. He, Y.-S. Liu, *Anal. Chem.* **1999**, *71*, 3873–3876.
- [57] a) T. J. Melton, J. Joyce, J. T. Meloy, J. A. Boon, J. S. Wilkes, *J. Electrochem. Soc.* **1990**, *137*, 3865–3869; b) C. Scordilis-Kelley, J. Fuller, R. T. Carlin, J. S. Wilkes, *J. Electrochem. Soc.* **1992**, *139*, 694–699.
- [58] a) I. C. Quarmby, R. A. Mantz, L. M. Goldenberg, R. A. Osteryoung, *Anal. Chem.* **1994**, *66*, 3558–3561; b) I. C. Quarmby, R. A. Osteryoung, *J. Am. Chem. Soc.* **1994**, *116*, 2649–2650.
- [59] P. Koronaios, D. King, R. A. Osteryoung, *Inorg. Chem.* **1998**, *37*, 2028–2032.
- [60] B. Ellis, W. Keim, P. Wasserscheid, *Chem. Commun.* **1999**, 337–338.
- [61] a) G. P. Smith, A. S. Dworkin, R. M. Pagni, S. P. Zingg, *J. Am. Chem. Soc.* **1989**, *111*, 525–530; b) M. Ma, K. E. Johnson, *J. Am. Chem. Soc.* **1995**, *117*, 1508–1513.
- [62] C. L. Hussey, *Adv. Molten Salt Chem.* **1983**, *5*, 185–230.

- [63] J. Howarth, K. Hanlon, D. Fayne, P. McCormac, *Tetrahedron Lett.* **1997**, 38, 3097–3100.
- [64] a) A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, 113, 361–363; b) A. J. Arduengo, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, 114, 5530–5534; c) G. T. Cheek, J. A. Spencer in *9th Int. Symp. on Molten Salts* (Hrsg.: C. L. Hussey, D. S. Newman, G. Mamantov, Y. Ito), The Electrochem. Soc., New York, **1994**, S. 426–432.
- [65] L. Xu, W. Chen, J. Xiao, *Organometallics* **2000**, 19, 1123–1127.
- [66] M. Tinkl, *Chem. Rundsch.* **1999**, 2, 59.
- [67] Solvent Innovation GmbH (<http://www.solvent-innovation.com>).
- [68] a) M. Freemantle, *Chem. Eng. News* **1999**, 77, 23–24; b) D. Bradley, *Chem. Ind.* **1999**, 86; c) M. Freemantle, *Chem. Eng. News* **2000**, 78, 37–50.
- [69] P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza, J. Dupont, *Inorg. Chim. Acta* **1997**, 255, 207–209.
- [70] L. A. Müller, J. Dupont, R. F. de Souza, *Makromol. Chem. Rapid Commun.* **1998**, 19, 409–411.
- [71] a) B. Driessen-Hölscher, J. Heinen, *J. Organomet. Chem.* **1998**, 570, 141–146; b) J. Heinen, M. S. Tupayachi, B. Driessen-Hölscher, *Catalysis Today* **1999**, 48, 273–278.
- [72] S. Steines, B. Driessen-Hölscher, P. Wasserscheid, *J. Prakt. Chem.* **2000**, 342, 348–354.
- [73] A. L. Monteiro, F. K. Zinn, R. F. de Souza, J. Dupont, *Tetrahedron: Asymmetry* **1997**, 2, 177–179.
- [74] P. A. Chaloner, M. A. Esteruelas, F. Joó, L. A. Oro, *Homogeneous Hydrogenation*, Kluwer, Dordrecht, **1994**.
- [75] C. E. Song, E. J. Roh, *Chem. Commun.* **2000**, 837–838.
- [76] P. Wasserscheid, W. Müller, C. Werth, A. Jess, noch unveröffentlichte Ergebnisse.
- [77] Y. Chauvin, H. Olivier, L. Musmann, FR 95/14,147, **1995** [*Chem. Abstr.* **1997**, 127, P341298k].
- [78] C. C. Brasse, U. Englert, A. Salzer, H. Waffenschmidt, P. Wasserscheid, *Organometallics*, im Druck.
- [79] A. Salzer, C. C. Brasse, WO99/16776, **1999** [*Chem. Abstr.* **1999**, 130, 267580x].
- [80] W. Keim, D. Vogt, H. Waffenschmidt, P. Wasserscheid, *J. Catal.* **1999**, 186, 481–484.
- [81] D. E. Kaufmann, M. Nouroozian, H. Henze, *Synlett* **1996**, 1091–1092.
- [82] a) W. A. Herrmann, V. P. W. Böhm, *J. Organomet. Chem.* **1999**, 572, 141–145; b) V. P. W. Böhm, W. A. Herrmann, *Chem. Eur. J.* **2000**, 6, 1017–1025.
- [83] A. J. Carmichael, M. J. Earle, J. D. Holbrey, P. B. McCormac, K. R. Seddon, *Org. Lett.* **1999**, 1, 997–1000.
- [84] J. E. L. Dullius, P. A. Z. Suarez, S. Einloft, R. F. de Souza, J. Dupont, J. Fischer, A. D. C. A. N. *Organometallics* **1998**, 17, 815–819.
- [85] W. Chen, L. Xu, C. Chatterton, J. Xiao, *Chem. Commun.* **1999**, 1247–1248.
- [86] C. de Bellefon, E. Pollet, P. Grenouillet, *J. Mol. Catal.* **1999**, 145, 121–126.
- [87] a) R. B. A. Parry, I. Tkatschenko, *J. Chem. Soc. Chem. Commun.* **1981**, 49–50; b) J. R. Ascenso, M. A. A. F. De C. T. Carrando, A. R. Dias, P. T. Gomes, M. F. M. Piadade, C. C. Romao, A. Revillon, I. Tkatschenko, *Polyhedron* **1989**, 8, 2449–2457; c) P. Grenouillet, D. Neibecker, I. Tkatschenko, *J. Organomet. Chem.* **1983**, 243, 213–222; d) J.-P. Gehrke, R. Taube, E. Balbolov, K. Kurtev, *J. Organomet. Chem.* **1986**, 304, C4–C6.
- [88] a) I. Brassat, Dissertation, RWTH Aachen, **1998**; b) I. Brassat, U. Englert, W. Keim, D. P. Keitel, S. Killat, G.-P. Suranna, R. Wang, *Inorg. Chim. Acta*, **1998**, 280, 150–162.
- [89] P. Wasserscheid, C. Hilgers, W. Keim, noch unveröffentlichte Ergebnisse.
- [90] S. Einloft, F. K. Dietrich, R. F. de Souza, J. Dupont, *Polyhedron* **1996**, 15, 3257–3259.
- [91] a) Y. Chauvin, H. Olivier, C. N. Wyrvalski, L. C. Simon, R. F. de Souza, *J. Catal.* **1997**, 165, 275–278; b) L. C. Simon, J. Dupont, R. F. de Souza, *J. Mol. Catal.* **1998**, 175, 215–220.
- [92] a) E. Burridge, *ECN Chemscape* **1999**, 27–28; b) H. Olivier, *J. Mol. Catal.* **1999**, 146, 285–289.
- [93] Y. Chauvin, S. Einloft, H. Olivier, FR 93/11,381, **1996** [*Chem. Abstr.* **1995**, 123, 144896c].
- [94] G. Wilke, B. Bogdanović, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, H. Zimmermann, *Angew. Chem.* **1966**, 78, 157–172; *Angew. Chem. Int. Ed. Engl.* **1966**, 5, 151–164.
- [95] P. Wasserscheid, W. Keim, WO 9847616, **1997** [*Chem. Abstr.* **1998**, 129, 332457h].
- [96] M. Eichmann, Dissertation, RWTH-Aachen, **1999**.
- [97] a) P. Wasserscheid, M. Eichmann, *Proc. 3rd Int. Symp. Catal. in Multiphase Reactors*, Neapel, **2000**, S. 249–261; b) M. Eichmann, P. Wasserscheid, *Catal. Today*, eingereicht; c) M. Eichmann, P. Wasserscheid, unveröffentlichte Ergebnisse.
- [98] T. J. Gannon, G. Law, P. R. Watson, A. J. Carmichael, K. R. Seddon, *Langmuir* **1999**, 15, 8429–8434.

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

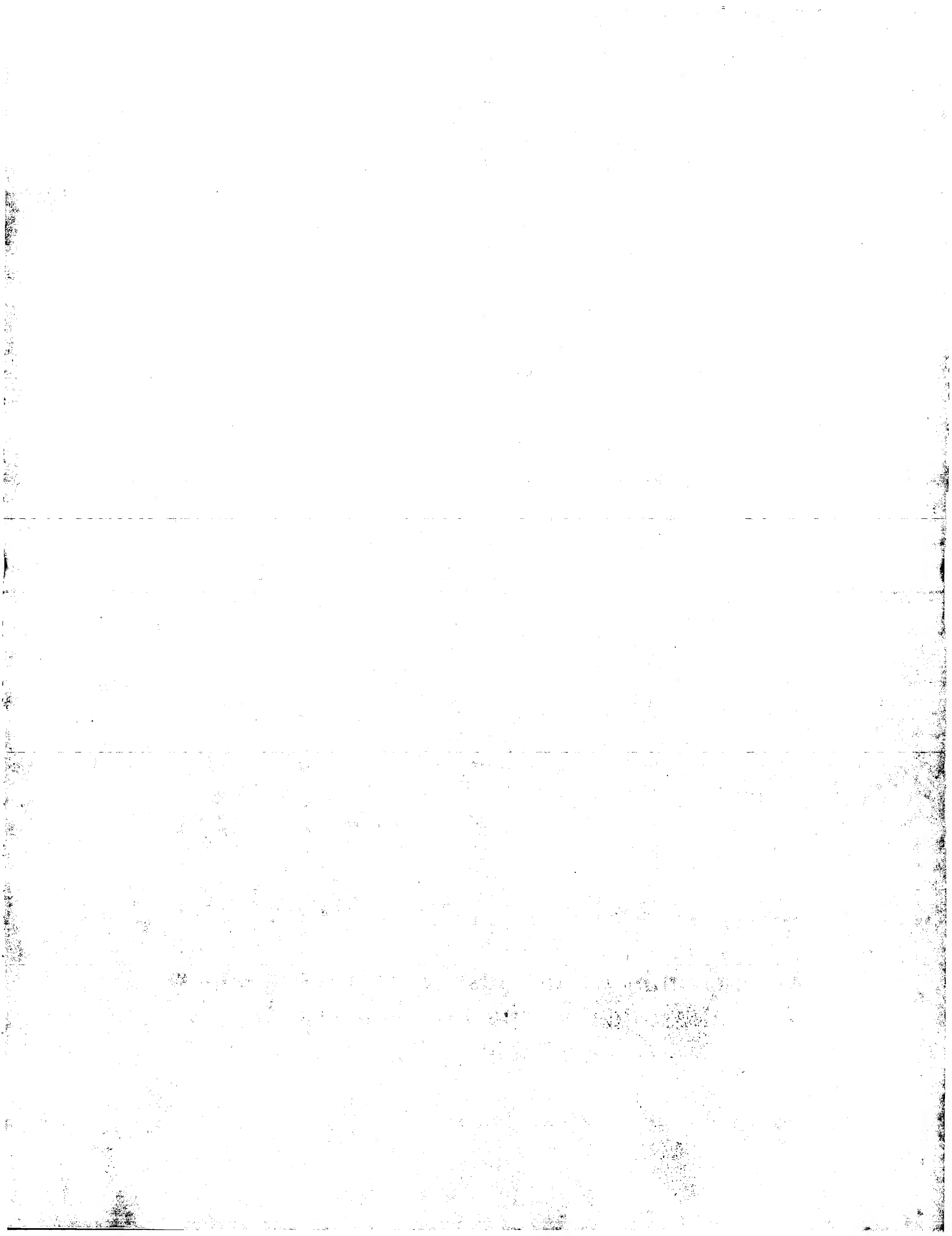
Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

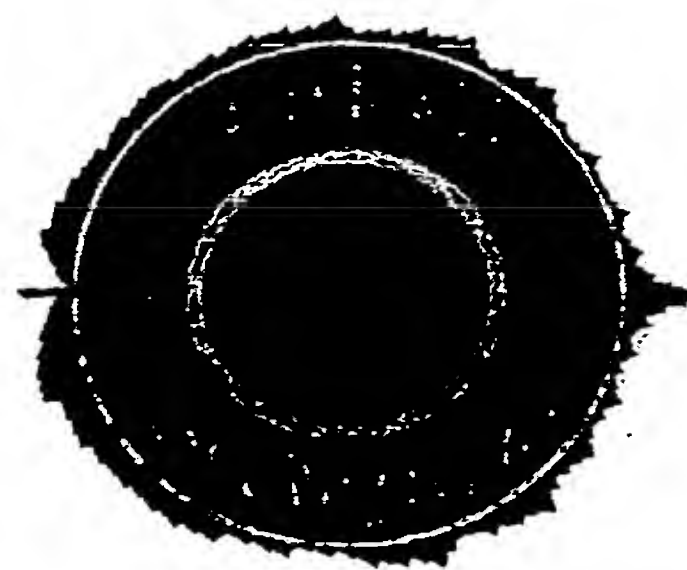
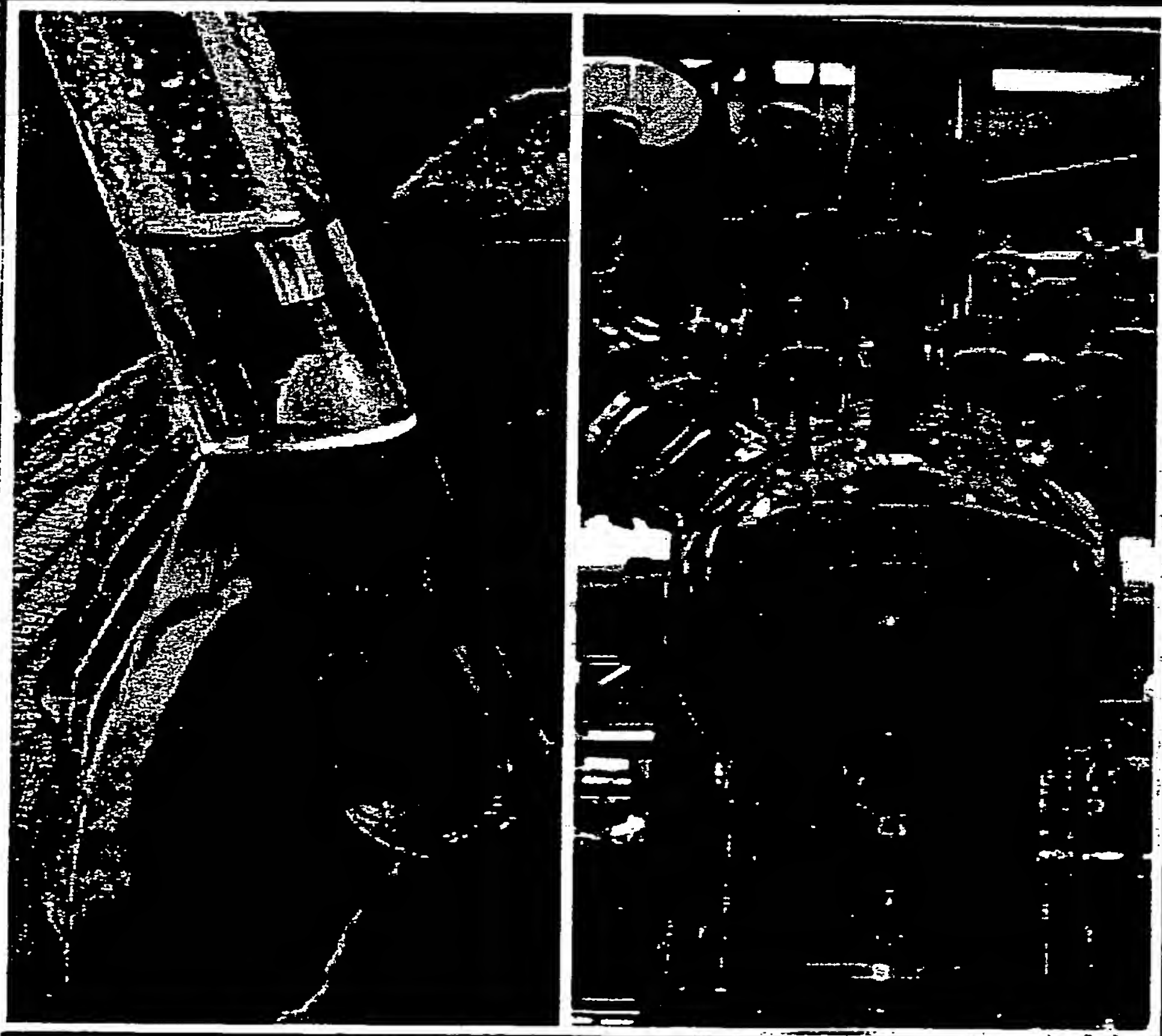
IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



Ionic Liquids in Synthesis

Peter Wasserscheid, Tom Welton (Eds.)



THIS PAGE BLANK (USPTO)

wide variety of anions ($[\text{PF}_6]^-$, $[\text{SbF}_6]^-$, $[\text{BF}_4]^-$, $[\text{ClO}_4]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{NO}_3]^-$, and $[\text{CF}_3\text{CO}_2]^-$). For the acetone route, $[\text{EMIM}]\text{Cl}$ was stirred with NH_4BF_4 or $\text{NH}_4[\text{CF}_3\text{SO}_3]$ at room temperature for 72 hours. In this case all starting materials were only slightly soluble in the reaction solvent. Once again, the insoluble NH_4Cl by-product was removed by filtration. No water wash was carried out, but trace organic impurities were removed by stirring the acetone solution with neutral alumina for two hours after removal of the metal halide salts by filtration. The salts were finally dried by heating at 120°C for several hours, after which they were analyzed for purity by electrochemical methods, giving quoted purities of at least 99.95 %.

2.1.4

Purification of Ionic Liquids

The lack of significant vapor pressure prevents the purification of ionic liquids by distillation. The counterpoint to this is that any volatile impurity can, in principle, be separated from an ionic liquid by distillation. In general, however, it is better to remove as many impurities as possible from the starting materials, and where possible to use synthetic methods that either generate as few side products as possible, or allow their easy separation from the final ionic liquid product. This section first describes the methods employed to purify starting materials, and then moves on to methods used to remove specific impurities from the different classes of ionic liquids.

The first requirement is that all starting materials used for the preparation of the cation should be distilled prior to use. The author has found the methods described by Amarego and Perrin to be suitable in most cases [44]. In the preparation of $[\text{RMIM}]^+$ salts, for example, we routinely distil the 1-methylimidazole under vacuum from sodium hydroxide, and then immediately store any that is not used under nitrogen in the refrigerator. The haloalkanes are first washed with portions of concentrated sulfuric acid until no further color is removed into the acid layer, then neutralized with NaHCO_3 solution and deionized water, and finally distilled before use. All solvent used in quaternization or anion-exchange reactions should also be dried and distilled before use. If these precautions are not taken, it is often difficult to prepare colorless ionic liquids. In cases where the color of the ionic liquids is less important, the washing of the haloalkane may be unnecessary, as the quantity of colored impurity is thought to be extremely low, and thus will not affect many potential applications. It has also been observed that, in order to prepare AlCl_3 -based ionic liquids that are colorless, it is usually necessary to sublime the AlCl_3 prior to use (often more than once). It is recommended that the AlCl_3 should be mixed with sodium chloride and aluminium wire for this process [22b].

AlCl_3 -based ionic liquids often contain traces of oxide ion impurities, formed by the presence of small amounts of water and oxygen. These are generally referred to as $[\text{AlOCl}_2]^-$, although ^{17}O NMR measurements have indicated that a complex series of equilibria is in fact occurring [45]. It has been reported that these can be efficiently removed by bubbling phosgene (COCl_2) through the ionic liquid [46]. In this

case the by-product of the reaction is CO_2 , and thus easily removed under vacuum. This method should be approached with caution due to the high toxicity of phosgene, and an alternative approach using the less toxic triphosgene has also been reported more recently [47]. In the presence of water or other proton sources, chloroaluminate-based ionic liquids may contain protons, which will behave as a Brønsted superacid in acidic melts [48]. It has been reported that these may be removed simply by the application of high vacuum ($< 5 \times 10^{-6}$ Torr) [49].

Purification of ionic liquids formed by anion metathesis can throw up a different set of problems, as already noted in Section 2.1.3.2. In this case the most common impurities are halide anions, or unwanted cations inefficiently separated from the final product. The presence of such impurities can be extremely detrimental to the performance of the ionic liquids, particularly in applications involving transition metal-based catalysts, which are often deactivated by halide ions. In general this is much more of a problem in water-soluble ionic liquids, as water-immiscible salts can usually be purified quite efficiently by washing with water. The methods used to overcome this problem have already been covered in the previous section. The problems inherent in the preparation of water-miscible salts have been highlighted by Seddon et al. [37], who studied the Na^+ and Cl^- concentrations in a range of ionic liquids formed by treatment of [EMIM]Cl and [BMIM]Cl with $\text{Ag}[\text{BF}_4]$, $\text{Na}[\text{BF}_4]$, $\text{Ag}[\text{NO}_3]$, $\text{Na}[\text{NO}_3]$, and HNO_3 . They found that the physical properties such as density and viscosity of the liquids can be radically altered by the presence of unwanted ions. The results showed that all preparations using Na^+ salts resulted in high residual concentrations of Cl^- , while the use of Ag^+ salts gave rise to much lower levels. The low solubility of NaCl in the ionic liquids, however, indicates that the impurities arise from the fact that the reaction with the Na^+ salts does not proceed to completion. Indeed, it was reported in one case that unreacted [BMIM]Cl was isolated by crystallization from [BMIM][NO_3]. A further example of the potential hazards of metal-containing impurities in ionic liquids is seen when [EMIM][CH_3CO_2] is prepared from [EMIM]Cl and $\text{Pb}[\text{CH}_3\text{CO}_2]_4$ [50]. The resulting salt has been shown to contain ca. 0.5 M residual lead [51].

In practical terms, it is suggested that, in any application where the presence of halide ions may cause problems, the concentration of these be monitored to ensure the purity of the liquids. This may be achieved either by the use of an ion-sensitive electrode, or alternatively by use of a chemical method such as the Vollhard procedure for chloride ions [52]. Seddon et al. have reported that effectively identical results were obtained with either method [37].

Most ionic liquids based on the common cations and anions should be colorless, with minimal absorbance at wavelengths greater than 300 nm. In practice, the salts often take on a yellow hue, particularly during the quaternization step. The amount of impurity causing this is generally extremely small, being undetectable by ^1H NMR or CHN microanalysis, and in many applications the discoloration may not be of any importance. This is clearly not the case, however, when the solvents are required for photochemical or UV/visible spectroscopic investigations. To date, the precise origins of these impurities have not been determined, but it seems likely that they arise from unwanted side reactions involving oligomerization or polymer-

ization of small amounts of free amine, or else from impurities in the haloalkanes. Where it is important that the liquids are colorless, however, the color may be minimized by following a few general steps:

- All starting materials should be purified as discussed above [44].
- The presence of traces of acetone can sometimes result in discoloration during the quaternization step. Thus, all glassware used in this step should be kept free of this solvent.
- The quaternization reaction should be carried out either in a system that has been degassed and sealed under nitrogen, or else under a flow of inert gas such as nitrogen. Furthermore the reaction temperature should be kept as low as possible (no more than ca. 80 °C for Cl⁻ salts, and lower for Br⁻ and I⁻ salts).

If the liquids remain discolored even after these precautions, it is often possible to purify them further by first stirring with activated charcoal, followed by passing the liquid down a short column of neutral or acidic alumina as discussed in Section 2.1.3.2 [33].

Clearly, the impurity likely to be present in largest concentrations in most ionic liquids is water. The removal of other reaction solvents is generally easily achieved by heating the ionic liquid under vacuum. Water is generally one of the most problematic solvents to remove, and it is generally recommended that ionic liquids be heated to at least 70 °C for several hours with stirring to achieve an acceptably low degree of water contamination. Even water-immiscible salts such as [BMIM][PF₆] can absorb up to ca. 2 wt.% water on equilibration with the air, corresponding to a water concentration of ca. 1.1 M. Thus it is advised that all liquids be dried directly before use. If the amount of water present is of importance, it may be determined either by Karl–Fischer titration, or a less precise determination may be carried out using IR spectroscopy.

2.1.5

Conclusions

It is hoped that this section will give the reader a better appreciation of the range of ionic liquids that have already been prepared, as well as a summary of the main techniques involved and the potential pitfalls. While the basic chemistry involved is relatively straightforward, the preparation of ionic liquids of known purity may be less easily achieved, and it is hoped that the ideas given here may be of assistance to the reader. It should also be noted that many of the more widely used ionic liquids are now commercially available from a range of suppliers, including some specializing in the synthesis of ionic liquids [53].

THIS PAGE BLANK (USPTO)

explanation, said control method is explained hereunder, referring to flow charts shown in Figs. 7 through 10. Fig. 7 shows the overall process of focusing, and each one of Figs. 8 through 10 shows in detail a part of the focusing process shown in Fig. 7.

As shown in Fig. 7, multiple image data is used to perform focusing. First, in order to obtain image data of an image focusing area W, one frame of a picture is taken for automatic focusing processing at the initial position or the current position of the lens (Step 101). Using the data of the photographed image, a contrast evaluated value for each window W1-W9 of the image focusing area W is calculated (Step 102). When calculating each contrast evaluated value, peak values of all the lines in the each respective window W1-W9 are summed up. Then, the average position of the subject T is calculated by finding relative positions of each of the peak values of all the lines in each window W1-W9 from a reference position in the each respective window W1-W9 and summing up these relative positions (Step 103). The number N of frames to be photographed is calculated (Step 104), and until N times of photographing actions are completed (Step 105), photographing actions are repeated while moving the lens of the optical system 11 (Step 105). In other words, lens moving and picture taking for focusing are repeated N times (Steps 101-106) to obtain

evaluated values of continuous image data.

In cases where the position of the lens driven in Step 106 is relatively close to the distance to the subject T, the average position calculated in Step 103 based on the image data captured for focusing in Step 101 sufficiently reflects the characteristics of the main contrast of the subject T. Therefore, especially in cases where camera shake or other incident causes movement of the subject in a window in which the camera position is close to the distance to the subject T, a change in the average of the peak positions is inevitable.

An explanation is now given of the process of calculating the number N of frames to be photographed for focusing (Step 104), referring to the flow chart shown in Fig. 8.

The purpose of setting the number N of frames to be photographed is to obtain sufficient essential image data by changing the number N of frames to be photographed based on the lens magnification of the optical system 11, the data of the distance to the subject T to be photographed, various photographing conditions set by the photographer, etc.

First, the evaluated value FV for each window W1-W9 calculated in Step 102 in Fig. 7 is compared with a given reference value FVTHn (Step 201). When the evaluated value FV is greater than the reference value FVTHn, N0 is input as N (Step 202). Step 201 may be omitted. N0 may be input as a variable

based on the focus magnification for N. When the evaluated value FV is not greater than the reference value FVTHn (Step 201) in a situation where close-up photography is or has been chosen (Step 203) by the photographer who is operating the image capturing apparatus 10, or where the focus magnification is relatively large (for example 2X or more) (Step 204), N2 is input as N (Step 205). Under conditions other than those described above, in other words when the evaluated value FV is not greater than the reference value FVTHn (Step 201) in a situation where short-range photography is not chosen (Step 203) and where the focus magnification is relatively small (for example less than 2X) (Step 204), N1 is input as N (Step 206). The values N0, N1, N2 are smaller in the indicated order ($N0 < N1 < N2$). To perform short-range photography or when the focus magnification is large, meticulous evaluation is enabled by setting a large number N of images to be captured to provide minute setting for driving the lens of the optical system 11. On the other hand, when the subject T is located close to the optical system 11 (for example, when the calculated evaluated value FV is greater than a given reference value FVTHn), duration of focusing can be reduced by setting a small number N of images to be captured. In short, by providing a means to selectively set the lens driving range based on an evaluated value, the duration of focusing can be reduced without impairing precision of

focusing.

As shown in Fig. 7, judgment is made as to whether there is camera shake or like affecting an average position of the peak positions obtained through the N times of photographing actions, and the amount of the weight, which represents the reliability, to be placed on each window W1-W9 is calculated (Step 111). Next, how the determining circuit calculates the amounts of the weights is explained in detail, referring to the flow chart shown in Fig. 9.

First, $K_p = PTH(\text{base})$, which represents an initial value of the moving distance of peak value average positions (PTH) is set beforehand (Step 301). Then, each window W_h of the image focusing area W, in which a number of scenes are captured, is examined to determine a single or plural scenes $S(H)W_h$ that presents the highest evaluated value (Step 302).

The peak value average position moving distance PTH is used as a final control value for selecting the amount of the weight on each window W_h . The peak value average position moving distance PTH is a variable that changes based on photographing conditions, such as the brightness, focal length, etc.

In cases where the brightness in a photographed scene is relatively high (Step 303), the moving distance in a window tends to be reduced because of an increased shutter speed.

Therefore, in order to reduce the peak value average position moving distance PTH to a level lower than the preset initial value $K_p = PTH(\text{base})$, the ratio $K(L)$ by which the initial value $PTH(\text{base})$ will be multiplied is set at, for example, 80% (Step 304). Should the brightness be not high, in other words, for example, should it be rather low (Step 303), the ratio $K(L)$ is set at, for example, 100% (Step 305). In cases where the focus magnification is relatively high (Step 306), there is a higher possibility of camera shake than when focus magnification is low. Therefore, in order to reduce the peak value average position moving distance PTH to a level lower than the preset initial value $PTH(\text{base})$, the ratio $K(f)$ by which the initial value $PTH(\text{base})$ will be multiplied is set at, for example, 80% (Step 307). Should the focus magnification be not high, in other words, for example, should it be rather low (Step 307), the ratio $K(f)$ is set at, for example, 100% (Step 308).

The peak value average position moving distance PTH, which serves as the most appropriate control value for the photographed scene, is calculated by multiplying the preset initial value $K_p = PTH(\text{base})$ by ratios $K(L), K(f)$, which have respectively been calculated as above based on the brightness and focus magnification (Step 309). In other words, calculation of the equation $PTH = K_p \times K(L) \times K(f)$ is done. According to the present embodiment, the peak value average

position moving distance PTH is calculated based on the brightness and focus magnification. However, in cases where it is possible to find the most appropriate control value beforehand, the initial value PTH(base) of the peak value average position moving distance PTH may be directly used as the peak value average position moving distance PTH.

Next, the reliability of each window W_h is calculated, which begins with initialization of an amount of weight, i.e. a weighting factor (Step 310). The weighting factor is represented in terms of proportion to 100%. For example, the weighting factor may be initialized at 100%. At the same time, a variable m is provided with respect to the calculated peak value average position moving distance PTH so that the weighting factor can be set as a variable. For example, in cases where the weighting factor can be set at four levels, m may be 4, 3, 2, or 1, with 4 being the initial value.

When determining the amount of the weight, the ratio to the calculated peak value average position moving distance PTH is set as a changeable value, i.e. a peak value average position moving distance $PTH(m)$, by using the variable m (Step 311). To be more specific, the peak value average position moving distance $PTH(m)$ is found by dividing the peak value average position moving distance PTH calculated in the previous step by the variable m .

When the difference in the absolute value between the peak value average position $\Delta PS(H)Wh$ in the scene $S(H)Wh$ and the peak value average position $\Delta PS(H-1)Wh$ in the previous scene $S(H-1)Wh$ is greater than the peak value average position moving distance $PTH(m)$, the CPU 17 serving as the determining means judges that camera shake or other similar incident has caused the subject T to move across windows W1-W9 or affected the calculation of the evaluated value (Step 312). When the difference in the absolute value between the peak value average position $\Delta PS(H)Wh$ in the scene $S(H)Wh$ and the peak value average position $\Delta PS(H+1)Wh$ in the subsequent scene $S(H+1)Wh$ is greater than the peak value average position moving distance $PTH(m)$, the determining means also judges that camera shake or other similar effect has caused the subject T to move across windows W1-W9 or exerted an influence on the calculation of the evaluated value (Step 313). In cases where neither difference in the absolute value exceeds the peak value average position moving distance $PTH(m)$, the determining means judges that there is neither camera shake nor an unfavorable influence on calculation of the evaluated value and, therefore, does not reduce the weighting factor for the pertinent window Wh. The greater the variable m, the smaller the peak value average position moving distance $PTH(m)$ used in comparison, making it more difficult to determine the peak value average position

moving distance. The weighting factors to be used are set based on the corresponding peak value average position moving distance $PTH(m)$ (step 315). Should the difference in the absolute value be found to be greater than the set peak value average position moving distance $PTH(m)$ in Step 312 or Step 313, the weighting for the corresponding window Wh is reduced by reducing the weight factor, which is based on the assumption that camera shake is present (Step 315). At that time, the weight factor may be reduced to, for example, as low as 25%. Comparison described above is repeated with the value of the variable m being reduced one at a time from the initial value, e.g. 4 (Step 316), until the variable m becomes 0 (Steps 311-317), while determining the amount of the weight based on each variable (314,315). Although the minimum weighting factor is set at 25% according to the present embodiment, the weighting factor is not limited to this particular value; for example, the minimum weighting factor may be set at 0%. Furthermore, according to the present embodiment described above, the peak value average position moving distance $PTH(m)$ is a proportion to the peak value average position moving distance PTH calculated in the previous step. However, a plurality of optimum control values set beforehand may be used if it is possible.

By thus determining whether there has been camera shake

by a plurality of criteria, the reliability can be exact and multiple levels.

The operation described above is repeated until calculation for every window W1-W9 is completed (Steps 301-318). By means of weighting described above, the reliability of each window W1-W9 is put into numerical form as a weighting factor.

By applying the process described above to the windows adjacent to the relevant window S(H)Wh, it can be ascertained whether there has been any influence of camera shake or other movement of the target that forms a peak. To be more specific, after the weighting factor, i.e. reliability, of each window Wh is calculated as shown in Fig. 7, Eval FLG is set at 0 (Step 112). Thereafter, in cases where the number of windows Wh with a weighting factor or reliability of at least 100% is not less than a given level, e.g. 50% of all the windows (Step 113), or in cases where there are adjacent windows Wh, each of which has a reliability of not less than a given level, e.g. 100% (Step 114), the determining means judges that there is no movement of the subject T in the pertinent scene. Therefore, without performing weighting of evaluation which will be described later, the determining means performs validity determination by comparing the evaluated value with a preset control value (Step 117).

Should neither condition stipulated in Step 113 or 114

be fulfilled, calculation using weighting factors is performed as described hereunder. After the weighting factors for the windows W1-W9 are calculated, the entire evaluated values of each window W1-W9 are multiplied by the weighting factor calculated for the corresponding window so that weight on each evaluated value reflects on the evaluated value itself (Step 115). At that time, in order to show that calculation using a weighting factor has been performed, Eval FLG is set at 1 (Step 116).

Then, each weighted evaluated value is compared with a preset control value VTH to determine whether it is greater than the control value (Step 117). Thus, a process to determine whether it is valid as an evaluation target (Step 118) or invalid (Step 119) is conducted for every window W1-W9 (Steps 117-120).

Should a plurality of windows found to be valid, the CPU 17 finds a focusing distance by performing focusing distance calculation based on focusing positions, i.e. partial focusing distances, of the valid windows (Step 121).

The focusing distance calculation is shown in detail in Fig. 10. First, whether calculation using a weighting factor has been performed is determined from the state of Eval FLG (Step 401). In cases where weighting has been performed, the weighted evaluated values are summed up at each distance (Step 402). In cases the evaluated values have not been weighted, summation

is not performed. Peak focusing positions, i.e. peak positions, are calculated from the evaluated values (Step 403). In cases where all the peak focusing positions are outside a given photographing range, i.e. a linking range (Step 404), or every peak focusing position has a reliability not higher than a given level, e.g. 25% (Step 405), it is judged that calculation of the subject distance is impossible. In this case, the focusing position, i.e. the focal point at which the lens will be focused, is compelled to be set at a given value, which has been set beforehand (Step 406). At that time, focusing distance determination is judged to be NG (Step 407).

In a situation other than the above, in other words, in cases where one or more peak focusing positions (peak positions) are in the given photographing range (Step 404) and such peak focusing position(s) have a reliability greater than a given level, e.g. 25% (Step 405), it is judged that calculation of the subject distance is possible and, from among the valid windows W1-W9, the partial focusing position having the peak position at the closest focusing distance is chosen as the focusing position (Step 408). At that time, focusing distance determination is judged to be OK (Step 409).

When the focusing distance calculation described above includes weighting, the evaluated values are summed up in Step 402 to produce a single evaluated value so that the resulting

peak position represents the position of the center of gravity of plural evaluated values. However, the invention is not limited to such a configuration; it is also possible to choose only the windows whose peak positions are at a close distance, perform summation for each window, then calculate the partial focal point position, and set it as the focusing position. In cases where weighting has not been performed, it is also possible to choose the partial in-focus position at the closest distance from the windows W1-W9 that hold valid evaluated values, and set the partial focal point position as the focusing position.

Based on the result of determination of focusing distance, (Step 407 or 409) which has been obtained by the focusing distance calculation described above (Step 121), judgment is made as to whether the result of focusing distance determination is OK or NG as shown in Fig. 7 (Step 122). If the result is OK, the lens of the optical system 11 is moved to the set focusing position (Step 123). In case of NG, the lens of the optical system 11 is moved to the aforementioned preset focusing position (Step 124). Thus, the lens can be positioned at the final focusing position.

The device described above is an automatic focusing device used in an image capturing apparatus, such as a digital camera or a video camera and uses image data to perform automatic

focusing by a method which calls for dividing a frame into a plurality of areas and determining a focusing position in each area. Even for a scene containing an obstruction to range finding, such as movement of the subject or camera shake, the device according to the embodiment is capable of appropriate range finding and focusing the optical system 11 by detecting blur and using only the optimal data.

To be more specific, when peaks of evaluated values for respective plural areas have been calculated, a conventional device may simply use as the focusing position the partial focal length that is the focusing position at which the highest evaluated value has been recorded. However, by means of evaluated value weighting that takes into account the reliability of the evaluated values, the device according to the invention eliminates partial focal lengths obtained from windows having low reliability due to camera shake or other causes, uses only reliable evaluated values, even if they are not the highest values, to make a judgment and selects the partial focal length at the closest distance from among the evaluated values that have been ascertained to be valid. By using this method, which increases the probability of accurate focusing, the device is capable of making accurate judgment of the focusing position and thereby enables in-focus photography. The device according to the embodiment is particularly valid

when used in an optical system 11 of a so-called high-magnification type having a high zooming ratio.

Should the evaluated values themselves prior to weighting be low (e.g. evaluated values affected by noises or other factors or evaluated values in windows in which there is no valid subject), the embodiment is capable of accurate detection of the focal length by treating such windows to be invalid.

To be more specific, giving priority to the short range when calculating a plurality of focal lengths in a plurality of areas is a method generally deemed effective. However, should there be an erroneous peak at a distance shorter than the subject distance due to movement of the subject or camera shake, giving priority to the short range through a conventional process may prevent the location of the subject from being recognized as the focusing position and, instead, cause the erroneous peak to be determined as the focusing position, resulting in failure in setting the correct focusing position. Even if there is an erroneous peak at a distance shorter than the subject distance due to movement of the subject or camera shake, the device according to the embodiment is capable of detecting the movement of the subject or camera shake and using only the optimal data and thereby reliably setting an appropriate focusing position while giving priority to the

short range.

There is a conventional method that calls for correcting blur of an image of the subject or camera shake by changing the image detecting area and performing evaluation of the focal point again after the change of the image detecting area. Such a method presents a problem in that it takes a long time to complete calculation of the focusing position, resulting in a missed picture-taking opportunity. The constitution described above, however, enables rapid processing and capture of the shutter release moment, because the focusing position is calculated solely from the information obtained from preset image detecting areas.

By eliminating the need of an acceleration sensor or any other special device or equipment for detecting blur of an image of the subject or camera shake, the embodiment simplifies the structure of the automatic focusing device and thereby reduces its production costs.

By increasing the reliability of the calculated plural subject distances, the embodiment makes it possible to devise other algorithms.

As a focal point position is calculated based on evaluated values obtained from preset image detecting areas, the user can avoid any discomfort that would otherwise be felt from the lens focusing on an untargeted subject.

As the device is not affected by change in the brightness of images having flicker from such sources as a fluorescent lamp or the like and is therefore free from the problem of fluctuation in peak positions of evaluated values of the image, the device according to the embodiment is capable of evaluating the reliability of each one of the plural areas regardless of each evaluated value.

The embodiment described above employs a so-called hill-climbing search range finding method, which calls for obtaining evaluated values at a plurality of positions while operating the optical system 11, and recognizing a peak at the point when the curve of evaluated values changes from upward to downward. Should blur of a subject image occur, the peak position of each window moves inside the window and then into an adjacent window W1-W9. When the peak position of the contrast of the subject T moves from one window to another, the peak value of the evaluated values for the first-mentioned window decreases sharply. By reducing the weight on any window of which there has been a sudden change in the evaluated values with respect to a scene captured previously or immediately afterwards, the embodiment ensures elimination of data containing influence of camera shake and enables the accurate range finding and focusing, using only the most appropriate data.

The method described above calls for summation of the peak positions of the evaluated values. There is a variable in the peak positions of a relatively unfocused image. Therefore, according to the above method, the weight can be reduced when given to a window having a wide variable in the peak positions or having low peak values from the beginning.

As described above, at each change of the lens position of the optical system 11, the focusing device using the above method measures either the difference between peak values of evaluated values in the same window or the difference in the moving distance between the average position of the peak positions in one window and the average position of the peak positions in an adjacent window, or measures both kinds of differences. By performing this measurement, the device determines the reliability of the evaluated values of the pertinent window, thereby increasing the reliability of the window. Therefore, in cases where the short range is selected from among focal point positions in a plurality of areas at the time of deciding a final focusing position, range finding is performed with an increased reliability even if camera shake or movement of the subject should occur.

With the features as above, even if there is blur of the subject, the reliability of focusing can be increased.

Although the invention is explained referring to the

constitution that copes with horizontal movement of a subject T, the invention is also applicable to devices that cope with vertical or diagonal movement of a subject or any combination of these movements.

The image processing circuit 15 shown in Figs. 1 and 2 may be formed of the same chip as that of another circuit, e.g. the CPU 17, or executed by the software of the CPU 17. By thus simplifying the circuits, their production costs can be reduced. The filter circuits 32 of the image processing circuit 15 may be in any form, provided that they are capable of detecting contrast.

The range finding is not limited to the aforementioned hill-climbing search method and may be executed by scanning the entire range in which the automatic focusing device can operate.

Other than the procedure described above, it is also possible to sum up the evaluated values of a plurality of adjacent windows, after the weighting process shown in Fig. 9. Weighting may also be performed after summation of the evaluated values for a plurality of selected windows.

According to the method described above, one each value is set as the peak value average position moving distance PTH and the control value VTH for the process shown in Figs. 7 and 9. However, it is also possible to determine these values by selecting from among a plurality of preset values. Furthermore,

these values may vary depending on the largeness of the evaluated values or various photographing conditions including the brightness and data of the optical system 11, such as the shutter speed, focus magnification, etc. If such is the case, the optimal values may be selected based on these conditions or found by calculation using these conditions and data as variables in order to perform evaluation suitable for each scene.

When taking a picture using an electronic flash, by obtaining image data of respective scenes with the electronic flash emitting light in sync with each picture taking for focusing, a focusing distance can be detected by the focal length detecting method described above. When an electronic flash is used together with a device according to the invention, photographing is performed under control of light emission from the electronic flash based on the focusing distance and control of quantity of light, i.e. control of the aperture of the camera, shutter speed, etc.

The method described above chooses the partial focal length at the closest distance, i.e. the partial focusing position having the peak position at the closest distance, from among the valid evaluated values, and sets such a partial focusing position as the focusing position (Step 408). However, the invention is not limited to such a process; in accordance

with the intention of the user (to be more specific, in response to operation by the user, i.e. the photographer, to select the photographing mode), a partial focusing position other than the closest partial focusing position may be selected as the focusing position directly by the photographer or automatically as a result of selecting function of the control means in response to operation by the photographer. Furthermore, according to the method, when the result of focusing distance determination is NG (Step 122), the lens of the optical system 11 is moved to a preset focusing position (Step 124). However, it is also possible to set a plurality of focusing positions beforehand and move the lens of the optical system 11 to one of the present focusing positions in accordance with the intention of the photographer, i.e. operation by the photographer to select the photographing mode.

The focal length detecting method described above calls for setting a plurality of image detecting areas adjacent to one another, obtaining multiple image data while changing the focal length of an optical system, calculating from said multiple image data a partial focal length for each image detecting area based on which image data the peak value of contrast evaluated values has been recorded in, calculating the reliability of each image detecting area based on the position at which said peak value has been recorded moving across the

multiple image data, and selecting a focal length from a group consisting of said partial focal lengths and at least one given focal length, said focal length selected based on the reliability and the evaluated values of each respective image detecting area. As each reliability is calculated based on the position at which the peak value of the contrast evaluated values has been recorded moving across the multiple image data so that the partial focal length of an image detecting area that has a low reliability due to relative movement of the subject is excluded from selection, the method described above enables the accurate detection of the focal length.

According to the focal length detecting method, weighting of evaluated values is performed based on the calculated reliability, and a focal length is selected from among the partial focal lengths of the image detecting areas based on the evaluated values thereof to which weighting has been applied. By using evaluated values to which weighting has been applied based on a calculated reliability so that the partial focal length of an image detecting area having a low reliability is excluded from selection, the method described above enables the accurate detection of the focal length.

According to the focal length detecting method, should a position at which a peak value has been recorded move from at least one image detecting area that contains said position

into at least one other image detecting area, the reliability of the first-mentioned image detecting area is reduced. With the feature described above, the aforementioned method enables the accurate detection of the focal length by excluding the partial focal length of an image detecting area having a low reliability due to relative movement of the subject from selection.

According to the focal length detecting method, should a position at which a peak value has been recorded move more than a given distance across plural image detecting areas that contain said positions at which peak values have been recorded, the reliability is reduced. With the feature described above, the aforementioned method enables the accurate detection of the focal length by excluding the partial focal length of an image detecting area having a low reliability due to relative movement of the subject from selection.

According to the focal length detecting method, in cases where image data containing a great peak value has been obtained, the number of images to be subsequently obtained as data is reduced. With the feature described above, the method enables the reduction of time needed for focusing by obtaining only sufficient essential image data.

According to the focal length detecting method, a peak position movement determining value, which is used at the time

of calculation of a reliability for determining whether a position at which a peak value has been recorded has moved is a variable calculated based on photographing conditions. With the feature described above, the method enables the detection of an appropriate focal length by setting a peak position movement determining value based on photographing conditions, thereby enabling calculation of a reliability factor more appropriate for the photographing conditions.

According to the focal length detecting method, a plurality of peak position movement determining values are set for determining at the time of calculation of a reliability whether a position at which a peak value has been recorded has moved, and the peak position movement determining values are sequentially compared with the multiple image data. By setting a plurality of peak position movement determining values and sequentially comparing these values with the image data, the method having this feature enables the setting of reliability in a plurality of levels and thereby ensures detection of an appropriate focal length.

The focusing device described above comprises an image pickup device, an optical system for forming an image on the image pickup device, an optical system driving means for changing the focal length of the optical system, and an image processing means for processing image data output from the image

pickup device and controlling the optical system driving means, wherein the image processing means is adapted to obtain multiple image data while changing the focal length of the optical system by controlling the optical system driving means, define a plurality of image detecting areas adjacent to one another in each one of the multiple image data obtained as above, calculate a partial focal length for each image detecting area based on which image data the peak value of contrast evaluated values has been recorded in and also calculate the reliability of each image detecting area based on the position at which said peak value has been recorded moving across the multiple image data, and select a focal length from a group consisting of said partial focal lengths and at least one given focal length, based on the reliability and the evaluated values of each respective image detecting area. As each reliability is calculated based on the position at which the peak value of the contrast evaluated values has been recorded moving across the multiple image data so that the partial focal length of an image detecting area having a low reliability due to relative movement of the subject is excluded from selection, the device described above is capable of selecting an accurate focal length and appropriate focusing.

Next, a focal length detecting method and a focusing device according to the present embodiment of the invention are

explained, referring to Figs. 11 through 16.

This embodiment is based on the method described above and shown in Figs. 7 through 10. According to this embodiment, the photographer is allowed to select image data to be used for establishing the lens position, in other words final determination of the focal length. The photographer is enabled to make this selection automatically or manually from among RGB image data consisting of Red signals (R), green signals (G) and blue signals (B), in addition to brightness data, i.e. image data representing normal YCC brightness data. Furthermore, in addition to the short-range priority mode (the normal mode), which is a normal photographing mode, the photographer may also select the long-range priority mode; the photographer may even designate a desired range of photographing distance, i.e. a linking range, by means of a mode that can be called a far distance mode or an infinity mode. In the description hereunder, the explanation of the same elements or components as those of the constitution shown in Figs. 1 through 10 is omitted.

The device according to the present embodiment includes an operating means for determining whether selection of image data (brightness data or color data) to be used for determining the focal length is made automatically or manually by the photographer, an operating means for setting, in cases where manual operation has been selected, which color will be used

for determining the focal length, and an operating means which is a photographing mode selecting means to permit the photographer to choose the long-range priority mode or the far distance mode. Its function is similar to the function of focusing shown in the flow chart of Fig. 7 except that, as shown in Fig. 11, setting of a desired photographing mode (Step 11) and image signal determining processing (Step 12) are performed prior to taking a picture for automatic focusing processing (Step 101) and that the details for calculation of the reliability of each window (Step 111) and focusing distance calculation (Step 121) are different. Said calculation of the reliability of each window is performed in order to determine the amount of the weight to be placed on each evaluated value used for calculation of the focal length for the image data selected by the image signal determining processing.

First, an explanation is given of the process of setting the desired photographing mode. When focusing process involves designation of a range of photographing distance, it is necessary to know, as criteria for focusing, the range of photographing distance through the lens driving range based on the photographing modes of the image capturing apparatus 10. Should the photographing modes of the image capturing apparatus 10 include a normal mode which covers, for example, 50 cm to the infinity, the lens driving range is set for this mode. If

the image capturing apparatus 10 has other modes than the normal mode, such as a far distance mode (an infinity mode), a macro mode, etc., an operating means to enable the photographer to select any of these modes, in other words an operating means that enables the photographer to set the range of photographing distance, i.e. the lens driving range, is provided.

In the process of focusing, whether determination of the final focal length gives priority to the short range or the long range has to be decided as criteria for focusing. This is determined by the photographer selecting a photographing mode by operating the operating means of the image capturing apparatus 10. Should the photographing mode of the image capturing apparatus 10 be set at the long-range priority mode, setting is made to employ a longest-distance selecting mode for driving the lens so that the focusing distance corresponds to the longest distance in a captured image. In cases where the short-range priority mode has been selected, the focusing device is set at the shortest-distance selecting mode so that the focusing distance corresponds to the shortest distance in a captured image, thereby enabling photography with priority given to the short range, which is the mode generally employed.

The process of setting the desired photographing mode shown in Fig. 11 (Step 11) begins with ascertaining whether the photographer has designated the range of photographing distance

as shown in Fig. 12 (Step 1201). In cases where the mode for selecting the range of photographing distance has been selected, judgment is made as to whether the far distance photographing mode has been selected (Step 1202). In cases where the far distance mode has been selected, the longest-distance selecting mode is selected (Step 1203). In cases where the far distance mode has not been selected (in other words when either the macro mode or the normal mode has been selected), the shortest-distance selecting mode is selected (Step 1204). In short, the photographing mode, i.e. whether priority is given to the short range or the long range, is automatically decided in these steps based on the range of photographing distance.

In cases where the mode for selecting the range of photographing distance has not been selected in Step 1201, judgment is made as to whether long-range priority mode has been selected (Step 1205). If the photographer has selected the long-range priority mode, the longest-distance selecting mode is selected (Step 1203). In cases where the long-range priority mode has not been selected, the shortest-distance selecting mode is selected (Step 1204). In other words, the photographing mode that will determine the final focusing distance with priority on the intention of the photographer is selected in these steps.

The image signal determining processing (Step 12) shown

in Fig. 11 is for making selection between a manual mode and an automatic mode to be used in the focusing process from Step 11 to Step 106 in Fig. 11. The aforementioned manual mode is for the photographer to manually select brightness data or color data based on the subject or other conditions, whereas the automatic mode calls for the image capturing apparatus 10 to perform the selection automatically. The image signal determining processing, which is shown in Fig. 13 in detail, begins with ascertaining whether the photographer has chosen the manual mode for using either the brightness data or the color data from the image data information (Step 1301). In cases where the manual mode has been selected, judgment is made as to whether the photographer has chosen the mode for using the color data (Step 1302). In cases where the color data is not going to be used, the device is automatically switched to the mode for using only the brightness data (Step 1303). As the RGB color data is not going to be used, the variable CN is stored as 1 (CN=1) (Step 1304). In cases where the mode for using the color data rather than the brightness data for focusing has been selected in Step 1302, the device is enabled to put into numerical form a desired amount of weight to be placed on the color data of each RGB color. The numerical values will be used as set values in calculation of a focal length (Step 1305). For example, in cases where selection has been made so as to use

the color data of the three RGB colors, the variable CN, which represents the number of color data items, is stored as 3 (CN=3) (Step 1306). Settings of the matrix complementary circuit 27 and the switch 28 shown in Fig. 2 are made based on setting of the color data or the brightness data, such as the variable CN described above.

In cases where the manual mode has not been selected in Step 1301, the device functions in the automatic mode for automatically selecting color data or brightness data. In the automatic mode, the first procedure is to examine the value of brightness in the photographing environment (Step 1307). Should the current brightness value LV be lower than a preset brightness value LVTH, it is decided that the brightness data alone should be used as the image data for focusing due to the lack of color data, resulting in the subsequent progression to Step 1303. In cases where availability of the color data has been ascertained in Step 1307, weighting factors for the respective RGB colors are automatically set based on various settings, such as the photographing mode set in Step 11.

In cases where a white balance follow-up mode has been chosen (Step 1308), the weights on the information of each RGB color is automatically set based on the current information regarding the subject, such as the color data and the white balance WB (Step 1309). For example, in cases where it has been

judged that the subject contains a relatively large amount of red (R), the weights to be placed on evaluated values are calculated so that a greater value is set as a weight on R while relatively small values are set as the weighting factors for green (G) and blue (B).

Although it is not shown in the drawings, in cases where setting of a plurality of image areas is permitted, it is also possible to detect color data in each one of the image areas and set a great weight on the color with the greatest value.

Furthermore, weights on evaluated values may be set so as to deal with any one of a plurality of photographing modes other than those set in Step 11 (Step 1310).

For example, in the case of the present embodiment, which is provided with an auxiliary light device 23, based on the settings for control of light emission from the auxiliary light sources L1,L2 by the auxiliary light device 23 (Step 1311), the prescribed weight for each respective RGB color data is set either automatically or manually (Step 1312,1305). An auxiliary light determining processing, which controls the auxiliary light sources L1,L2, is explained in detail, referring to Fig. 14. When selecting the photographing mode, the photographer can choose whether to cause the auxiliary light sources L1,L2 to emit light manually or automatically (Step 1401). In cases where the manual mode has been selected in Step

1401, a single light source or a combination of light sources L1,L2 are selected from among the plurality of auxiliary light sources L1,L2 of auxiliary light device 23 of the image capturing apparatus 10 so that the selected light source(s) L1,L2 will emit light in accordance with the selection of the photographer (Step 1402). In cases where the manual mode has not been selected in Step 1401, the device functions in the automatic mode to automatically cause the auxiliary light source(s) L1,L2 to emit light when it is necessary(Step 1403). Whether or not light emission from the auxiliary light source(s) L1,L2 is necessary is judged by the CPU 17 based on the brightness data or other relevant information. When automatically causing the auxiliary light source(s) L1,L2 to emit light, the CPU 17 performs calculation based on information of the subject, such as brightness data or color data (Step 1404), to make judgment as to what color of auxiliary light L1,L2 is appropriate. As a result of the automatic calculation or the manual setting, judgment is made as to whether light emission from a plurality of auxiliary light sources L1,L2 is necessary. In cases where light emitted from a single auxiliary light source L1,L2 is sufficient, the optimal amount of weight to be placed on the evaluated value of each RGB color data is selected to obtain the maximum evaluated value (Step 1408 or 1409) based on the color data of the light from the selected auxiliary light

source L1,L2, i.e. either the first auxiliary light source L1 (Step 1406) or the second auxiliary light source L2 (Step 1407).

It is also possible to use three or more auxiliary light sources L1,L2...LN and set an appropriate weight for each respective auxiliary light source L1,L2...LN (Steps 1410,1411). Should the color data of each auxiliary light source L1,L2...LN remain undetermined, it must be processed as an error. If such is the case, the amount of the weight is set as if it were set for the first auxiliary light source L1, which is the normal auxiliary light source (Step 1408). The process when a plurality of auxiliary light sources L1,L2 are caused to emit light either manually or automatically (Step 1405) is now explained. For example, when causing the first auxiliary light source L1 and the second auxiliary light source L2 to emit light simultaneously (Step 1412), the optimal amount of weight to be placed on the evaluated value of each RGB color data is selected to obtain the maximum evaluated value (Step 1413) based on the color data of the light resulting from simultaneous light omission from the auxiliary light sources L1,L2. When causing an N number of auxiliary light sources L1,L2...LN in combination to emit light (Step 1414), the amount of the weight for each respective auxiliary light source L1,L2...LN to obtain the optimal result of the combination of these auxiliary light sources is selected (Step 1415) in the same manner as in the

case of causing a combination of two auxiliary light sources L1,L2 to emit light. Should the color data of the combination of auxiliary light sources L1,L2...LN remain undetermined, it must be processed as an error as is the case of a single auxiliary light source L1,L2...LN emitting light. If such is the case, the amounts of the weights are set as if the combination of the lights sources consisted of the first and second auxiliary light sources L1,L2, which is the normal combination of auxiliary light sources (Step 1413). When at least one of the auxiliary light sources L1,L2...LN is going to be caused to ultimately emit light, the variable LweightFlg is stored as 1 (Step 1416). When none of the auxiliary light sources L1,L2...LN is going to emit light, the variable LweightFlg is stored as 0 (Step 1417). Then, the auxiliary light determining processing returns to the flow chart shown in Fig. 13. In cases where light is emitted from at least one of the auxiliary light sources L1,L2...LN in the photographing mode (Step 1304) in the flow chart shown in Fig. 13, the variable LweightFlg is used for determining whether the setting of the amount(s) of the weight(s) described above has been completed.

In cases where light emission from the auxiliary light sources L1,L2...LN is not selected (Step 1311), and the photographing range is short, in other words when performing macro photography (Step 1313), it can be assumed that the color

data of the subject contains relatively vivid colors. Therefore, the amount of the weight for every RGB color data is set so that each RGB color is given a great weight (Step 1314).

Should the target of the photograph be limited to a specific subject, the amounts of the weights are set so as to facilitate focusing on the subject and also substantially reduce the possibility of focusing on the colors of any other objects that are expected to be near the subject. For example, should a mode for specifying flowers as the subject have been chosen (Step 1315), the weight on green (G) is reduced (Step 1316) in order to prevent erroneous focusing on green leaves rather than the flower that is the targeted subject.

In cases other than any of the ones previously discussed, to be more specific, in cases where none of the modes for tracking color temperature or white balance has been selected (Step 1308), and no specific photographing mode is set, in other words, in the case of what is referred to as a no-setting mode (Step 1310), a preset weight is set (Step 1317), and the variable CN, which represents the number of color data items, is stored as 3 (CN=3) (Step 1306). With the non-specific mode, a weight may be set so as to facilitate focusing on, for example, human skin color.

As described above, preset amounts of weights are set in Steps 1309, 1312, 1314, 1316, 1317, 1408, 1409, 1411, 1413 and 1415 in the image signal determination processing and the

auxiliary light determining processing shown in Figs. 13 and 14. Based on the color data or the brightness data set in the manner described above, color data or brightness data is set in the matrix complementary circuit 27 and the switch 28 shown in Fig. 2.

After the process from Step 101 to Step 120 shown in Fig. 11 is completed, the final focusing calculation in the focusing process is determined based on the selected photographing mode.

The process from Step 11 to Step 106 is repeated to obtain evaluated values of one set of continuous image data. In cases such as when there are a plurality of color data items, a plurality of sets of evaluated values are obtained. If such is the case, in order to process the plurality of sets of evaluated values, the process of calculation of the reliability of each window in Step 111 and the process of multiplication of the weight on each evaluated value in Step 115 are different from those of the constitution shown in Fig. 7.

To be more specific, the weight on each evaluated value obtained from image data containing brightness data or color data selected as above can be set in step 111 shown in Fig. 11, i.e. the process shown in Fig. 15. However, should there be a plurality of color data items of the image data, the evaluated value for each window Window(Wh) is calculated by using the color data CN, which has been stored beforehand. First, in the

same manner as the process shown in Fig. 9, a series of processes from Step 301 to Step 318 shown in Fig. 15 are conducted in the same manner as the processes shown in Fig. 9. The value CNB is then calculated from the equation $CNB = CN - 1$ (Step 319). Thereafter, the evaluated value Window(Wh) that has been calculated as above is replaced with the amount of the weight Window(Wh) (CNB) (Step 320). Should the calculated result of the value CNB be 0 (Step 321), it is obvious that either brightness data alone or color data of a single color is sufficient. Therefore, the value of the amount of the weight Window(Wh) (CNB), which has replaced the evaluated value Window(Wh) in Step 320, is stored as a calculated result of reliability (Step 322). In the case of $CN=3$, calculation of an amount of weight Window(Wh) (CNB) is repeated until processing of the color data for all three colors is completed. After calculation of all the sets of evaluation values, in other words, calculation for all the colors, is completed, the amounts of the weights Window(Wh) (CNB) for the color data of the evaluated values Window(Wh) for the respective windows are stored (Step 322).

After the process from Step 112 to Step 114 in the flow chart shown in Fig. 11 is completed, calculation is performed by multiplying the evaluated values by the weights by using the amounts of the weights Window(Wh) (CNB) for the color data of

the evaluated values Window(Wh) for the respective windows (Step 115). This calculation is a process of multiplying each evaluated value by reliability, i.e. an amount of weight. In the case of the present embodiment, calculation is performed for each color data, because the color data evaluated value and its reliability have already been obtained for each window. Therefore, weighting calculation for an evaluated value Window(Wh) of each window is performed based on the equation:

$$\text{Evaluated value (Wh)} = \Sigma \{ \text{FocusValue(CNB)} \times \text{Window(CNB)} \} / \text{CNB}$$

However, in the case of CN=1, the calculation is performed in the same manner as Step 115 shown in Fig. 7.

The entire evaluated values of each window W1-W9 are multiplied by the evaluated value (Wh) that has been found as above.

After the process from Step 117 to Step 120 shown in Fig. 11 is completed, focusing distance calculation shown in Fig. 16 is performed in step 121, instead of the steps shown in Fig. 10.

First, in the same manner as the process shown in detail in Fig. 10, whether calculation using a weighting factor has been performed is determined from the state of Eval FLG (Step 1601). In cases where weighting has been performed, the weighted evaluated values are summed up at each distance (Step

1602). In cases the evaluated values have not been weighted, summation is not performed. Peak focusing positions, i.e. peak positions, are calculated from the evaluated values (Step 1603). In cases where the photographing range, i.e. the linking range, has been set based on the photographing mode selected in Step 11 shown in Fig. 11 (Step 1604), should all the peak focusing positions be outside the preset photographing range (Step 1605), or every peak focusing position have a reliability not higher than a given level, e.g. 25% (Step 1606), it is judged that calculation of the subject distance is impossible (Step 1607). In this case, the focusing position, i.e. the focal point at which the lens will be focused, is compelled to be set at a given value, based on the photographing mode set in Step 11. The photographing mode is either the shortest-distance selecting mode or the longest-distance selecting mode. Therefore, in cases where calculation of the subject distance is judged to be impossible, it is determined whether the current mode is the longest-distance selecting mode (Step 1607). When the current mode is the longest-distance selecting mode, a given distance, i.e. Distance 1, is set (Step 1608). When the current mode is not the longest-distance selecting mode, another given distance, i.e. Distance 2, is set (Step 1609). Distance 1 is greater than Distance 2 (Distance 1 > Distance 2). At that time, focusing distance determination is judged to be NG (Step 1610).

Should every peak focusing position have a reliability not higher than a given level, e.g. 25% (Step 1606) in the situation where the linking range has not been set based on the photographing mode determined in Step 11 shown in Fig. 11 (Step 1604), calculation of the subject distance is judged to be impossible (Step 1607), and the same procedure as above is followed (Steps 1608-1610).

In cases other than the previously discussed Steps 1604-1605, to be more specific, in cases where the linking range has been set (Step 1604), one or more peak focusing positions (peak positions) are in the range of photographing distance that corresponds to the set photographing mode (Step 1605), and such peak focusing position(s) in the photographing range have a reliability greater than a given level, e.g. 25% (Step 1606), calculation of the subject distance is judged to be possible. In order to decide the peak position, which photographing mode has been selected in Step 11 is determined. Should the longest-distance selecting mode be the selected mode (Step 1611), the partial focusing position having the peak position at the longest distance is selected from among the valid windows W1-W9 and set as the focusing position (Step 1612). Should the longest-distance selecting mode be not the selected mode (Step 1611), in other words in cases where the current mode is the shortest-distance selecting mode, the partial focusing

position having the peak position at the shortest distance is selected from among the valid windows W1-W9 and set as the focusing position (Step 1613). At that time, focusing distance determination is judged to be OK (Step 1614).

Should there be at least one peak focusing position having a reliability higher than a given level, e.g. 25% (Step 1606) in the situation where the linking range has not been set based on the photographing mode determined in Step 11 shown in Fig. 11 (Step 1604), calculation of the subject distance is judged to be possible, and the same procedure as above is followed (Steps 1611-1614).

According to the result of focusing distance determination (Step 1610 or 1614) which has been obtained by focusing distance calculation described above (Step 121), as shown in Fig. 7, judgment is made as to whether the result of focusing distance determination is OK or NG (Step 122). If the result is OK, the lens of the optical system 11 is moved to the calculated focusing position (Step 123). In case of NG, the lens of the optical system 11 is moved to the aforementioned preset focusing position, i.e. Distance 1 or Distance 2 (Step 124). Thus, the lens can be positioned at the final focusing position.

As is described above, according to the present embodiment, use of color data when detecting a focal length

based on image data enables the correct detection of the focal length for a subject containing various color data in various photographing conditions. In other words, the embodiment increases the accuracy of focusing by providing a range finding method which calls for applying weight calculation to contrast evaluated values of the color signals of the image signals and thereby using only the optimal data and a focusing device using such a range finding method. Unlike a constitution that involves focusing based on evaluated values obtained by extracting only high-frequency components of brightness signals obtained from image data, using information other than brightness data, such as color data, enables the range finding for a subject, the distance to which cannot be measured from evaluated values of high-frequency components that have been extracted based only on difference in brightness. Therefore, the present embodiment enables the reduction of the types of subjects that present difficulties in focus control.

To be more specific, a focusing device according to the present embodiment has a means to detect contrast evaluated values for a plurality of color data, in other words contrast evaluated values for respective multiple image data obtained through at least two color filters of different colors, and a means (the matrix complementary circuit 27 and the switch 28) and processes (See Step 12 in Fig. 11) to make selection from

among said multiple image data and perform calculation on the selected image data, in addition to conducting a focusing process for each one of the multiple image data. The device according to the embodiment also has a means to perform weighting calculation for contrast evaluated values of each image data selected and processed by said means and processes.

According to the present embodiment, the amount of the weight of reliability of each evaluated data that has been obtained for each one of multiple image data is calculated for each one of the plurality of image detecting areas defined in each image data (See Steps 319-322 in Fig. 15).

Furthermore, calculation (See Step 115 in Fig. 11) is performed to apply weighting (See Step 111 in Fig. 11) to the evaluated values obtained based on the photographing mode (See Steps 11-12 in Fig. 11, Fig. 12 and Fig. 13). Then, based on the evaluated values to which weighting has been applied, a given focal length appropriate for the photographing mode is selected from among partial focal lengths of the image detecting areas.

Based on output color data or white balance signals, the image processing circuit 15 consisting of the CPU 17 and other components performs application (See Step 115 in Fig. 11) of weighting (See Step 111 in Fig. 11, Step 1309 in Fig. 13 and other relevant steps) to the obtained evaluated values and, by

using the evaluated values to which weighting has been applied, selects a given focal length appropriate for the photographing mode from among partial focal lengths of the image detecting areas.

A focusing device according to the present embodiment has a means to automatically (See the procedure from NO in Step 1301 onwards in Fig. 13) change over multiple image data (See the matrix complementary circuit 27, the switch 28 and Step 12 in Fig. 11) used for calculation of the focal length.

A focusing device according to the present embodiment has a means to manually (See the procedure from YES in Step 1301 onwards in Fig. 13) change over multiple image data (See the matrix complementary circuit 27, the switch 28 and Step 12 in Fig. 11) used for calculation of the focal length.

A focusing device according to the present embodiment has a means to automatically change over the image data containing the color data (See the matrix complementary circuit 27) used for calculation of the focal length based on the brightness of the subject (See Step 1307 in Fig. 13).

A focusing device according to the present embodiment has a means (See Steps 1301-1305 in Fig. 13) to enable the photographer to set a desired amount of weight (See Step 12 in Fig. 11) for each contrast evaluated value obtained from the image data (See the matrix complementary circuit 27, the switch

28 and Step 12 in Fig. 11) used for calculation of the focal length.

Furthermore, according to the present embodiment, evaluation is performed based on weighting, and a given focal length appropriate for the photographing mode is selected from among partial focal lengths of the image detecting areas.

As described above, because of inclusion of a means to select and process a single image signal or a plurality of different image signals from among a plurality of different image data, a means to perform focusing by using evaluated values of a focusing device according to the present embodiment is able to recognize the contrast of an image in wide range of situations, in other words, recognize the contrast of a subject image containing various color data under various photographing conditions. Furthermore, by applying weighting to evaluated values of each image data of a plurality of photographed images, the device according to the embodiment is capable of focusing calculation appropriate for the features of the subject.

As weighting is applied to evaluated values of each one of multiple image data based on color data or white balance, contrast is evaluated in accordance with the optimum criteria for the subject.

The embodiment also includes an automatic mode for automatically selecting multiple image data based on a subject.

Therefore, by using the automatic mode, the photographer can concentrate on taking pictures.

The embodiment also includes a manual mode for making selection of multiple image data manually. Therefore, by using the manual mode, the focusing process can directly reflect the photographer's intentions. As manual setting enables not only selection of image data but also direct setting of the amounts of the weights, which are essential for weight calculation in the focusing process, the manual setting enables focusing even under certain photographing conditions that would make focusing by a conventional constitution difficult.

As the manual mode includes a mode for permitting the photographer to select image data for focusing or set the amounts of the weights based on the selected photographing mode or other selection of conditions under which a subject is photographed, a focusing position that meets the photographer's expectation can be selected.

Conventional focusing processing that calls for calculation of a plurality of focal lengths in a plurality of areas and determination of the final focal length is performed by using brightness data alone or a single type of information that is similar to brightness data. However, by using evaluated values based on color data of different colors and applying weighting to these evaluated values with the photographer's

intention reflected in the weighting by setting a photographing mode or by any other means, the present embodiment enables accurate focusing. Furthermore, in the automatic mode, the constitution according to the present embodiment enables easy and accurate focusing by discerning features of the subject based on the color data and automatically weighting the evaluated values.

There may be occasions where a constitution that uses only a data of brightness or a single color is unable to detect contrast in an image having a uniform brightness even if the contrast is recognizable to the human eye because of color data. However, even under poor photographing conditions, such as when movement of the subject or camera shake is occurring in low-light condition, the use of data of a plurality of types selected from data of different colors and brightness enables the detection of contrast edges and also prevents erroneous recognition of a peak of evaluated values. Therefore, accurate focusing even on such a subject as one for which focusing is difficult by a conventional method or device is ensured.

When the photographer uses the manual mode in order to achieve focusing based only on color data of a specific color of a subject, the photographer can set the weights to be placed on the evaluated values based on spectral color data or brightness data of image data to be used for focusing. This

feature of the embodiment enables focus control that meets the photographer's expectation by permitting the photographer to select color data according to the specific color of the subject and set a desired weighting for each color data. For example, the color of a human face is not prone to be affected by other colors, although it has a relatively low contrast. In such a case, according to the present embodiment, it is possible to select color data or brightness data with the skin color being defined as a specific color and place a great weight only on the skin color when processing the evaluated values.

When taking a picture that includes flowers, should a photographer wishing to focus on the petals of a flower use only brightness data in the evaluation process, this may cause green leaves surrounding the flower petals to be erroneously detected as a peak of evaluated values, resulting in a failure to focus on the flower petals. The present embodiment is free from such a problem; in cases the flower petals are, for example, blue, using only blue color data for the evaluation process enables the focusing device to reliably recognize the flower petals as the targeted subject, ensuring reliable focusing on the blue petals even if it is outdoor shooting which is susceptible to subject shaking due to wind or other causes. As a photographing mode for calculating a focal length by using only image data that consists of color data of a specific color based on a subject

is thus provided, using only the image data that consists of the color data of a specific color ensures easy focusing on a subject on which the operator intends to focus on without being affected by other color data.

The present embodiment is provided with a brightness detecting circuit, auxiliary light sources L1,L2, and light source circuits 43,44 for respectively controlling the auxiliary light sources L1,L2. The brightness detecting circuit consists of the CPU 17 and other components and serves to measure brightness. The auxiliary light sources L1,L2 are a plurality of light sources adapted to support, based on brightness, photographing of images to obtain data for focal length detection. With the structure as above, control of light emission from the auxiliary light sources L1,L2 (See Steps 1406, 1407, 1410, 1412 and 1414 in Fig. 14) and weighting calculation (See Steps 1408, 1409, 1411, 1413 and 1415 in Fig. 14) are performed based on brightness data or color data (See Steps 1403 and 1404 in Fig. 14).

Furthermore, the embodiment includes what may be called a selective control enabling circuit (See the light source circuits 43,44 and the switches 45,46 in Fig. 2) for selecting any one or a plurality of light sources from among the auxiliary light sources L1,L2 and causing the selected auxiliary light source(s) L1,L2 to emit light simultaneously.

An auxiliary light determining means to make selection of auxiliary light sources L1,L2 is provided with a selecting means to control the auxiliary light sources L1,L2 either automatically or manually.

When selecting auxiliary light sources L1,L2 manually (See Step 1402 in Fig. 14), it is possible to perform weighting calculation (See Steps 1408, 1409, 1411, 1413 and 1415 in Fig. 14) based on color data of the light beams from the plurality of light sources L1,L2 (See Steps 1406, 1407, 1410, 1412 and 1414 in Fig. 14).

As described above, a plurality of auxiliary light sources L1,L2 are provided to support focusing. Therefore, even when photographing is performed in low-light conditions, the optimum focusing is ensured by using the auxiliary light sources L1,L2 so as to select the optimum image data from among multiple image data based on color temperatures and other characteristics of light from the auxiliary light sources L1,L2 and use the selected data for weighting calculation.

In other words, as the embodiment described above includes at least one auxiliary light source L1,L2, which is a light source to be used for focusing, and uses the auxiliary light source(s) L1,L2 for weighting evaluated values by causing the auxiliary light source(s) L1,L2 having the optimum color data of these auxiliary light sources L1,L2 to emit light and

selecting color data based on color temperatures or other features of the auxiliary light sources L1,L2. Therefore, the embodiment enables accurate focusing while effectively using the auxiliary light source(s) L1,L2. For example, when a red (R) light emitting diode (LED) is used as an auxiliary light source L1,L2, obtaining evaluated values from red color image data and giving a greater weight to red color data so that the auxiliary light reaches a farther distance at a lower cost than in a case where another color is used. As a result, accurate focusing is ensured even on a subject situated in a dark environment.

In cases where a plurality of auxiliary light sources L1,L2 are provided, the possibility of accurate focusing can be increased by selecting the auxiliary light source(s) L1,L2 to emit light based on features of the subject. For example, if three auxiliary light sources L1,L2,L3 (not shown) are provided and these auxiliary light sources L1,L2,L3 emit light beams of red, blue and green colors respectively, it is effective to select based on the color data of the subject the auxiliary light source L1,L2,L3 for emitting light of the color that is deemed to produce the most effective evaluated value and cause the selected auxiliary light source L1,L2,L3 to emit light.

With the configuration as above, wherein one or more

auxiliary light sources L1,L2 to emit light can be selected manually or automatically, the photographer can choose the optimum auxiliary light source L1,L2 based on conditions of the subject manually if he has knowledge of auxiliary light sources or automatically if he lacks such knowledge. In either way, the light source the most appropriate for the subject can be easily used for focusing.

Although the present embodiment described above uses RGB-type image data or YCC brightness data as information for obtaining evaluated values from image signals, it is also possible to generate image data of a specific color or color data in the form of CMY color difference consisting of cyan (C), magenta (M) and yellow (Y) by means of the matrix complementary circuit 27 shown in Fig. 2 and use the generated image data for processing. By using appropriate weight variables set based on information of these colors, an accurate focal length can be detected.

Furthermore, the present embodiment enables focusing to the long range side according to the intention of the photographer and thereby facilitates image capturing focused to the long range side as intended by the photographer. To be more specific, based on the range of photographing distance, the photographer can choose either the so-called normal mode or the mode aimed at far distance photography, e.g. the far

distance mode or the infinity mode, or, based on a constitution which enables the lens to be focused at any distance within the entire range of photographing distance for which the lens is designed, choose the mode that gives priority to either a short distance or a far distance. As a result of this feature, the photographer can take desired pictures easily. As a focusing position is determined using data which has been obtained from a plurality of image areas and ascertained to be free from any undesirable influence of sudden movement of the subject or the like, in other words data which has been judged to be valid for focusing, pictures can be taken that exactly meet the photographer's expectations. With the features as above, the present embodiment provides a method of automatic focusing which calls for dividing a frame into a plurality of areas and determining a focusing position in each area. Even with a scene containing an obstruction to range finding, such as movement of the subject or camera shake, the method according to the embodiment is capable of appropriate range finding and focusing of the optical system 11 by detecting blur and using only the optimal data, and, therefore is capable of increasing the accuracy of focusing.

Giving priority to the short range when calculating a plurality of focal lengths in a plurality of areas and determining a final focal length is a method generally deemed

effective. However, should there be an erroneous peak at a distance shorter than the subject distance due to movement of the subject or camera shake, giving priority to the short range through a conventional process may prevent the subject from being recognized as the focusing position and, instead, cause the erroneous peak to be determined as the focusing position, resulting in failure in setting the correct focusing position. When taking a picture of a subject located at a far distance rather than at a short distance, it is possible in this case too that movement of the subject or camera shake may cause an erroneous peak to be mistaken for the focusing position; the focusing position may be erroneously set at a peak located closer than the real peak or at a peak located even farther than the far distance intended by the photographer (for example, a position farther than the subject that is located farthest in the captured image). In either case, focusing is not done as the photographer intended. However, even if movement of the subject or camera shake generates an erroneous peak at a location closer or farther than the subject distance, the embodiment enables the reliable setting of an appropriate focusing position by detecting the movement of the subject or camera shake and using only the correct evaluated values while giving priority to the short range or long range based on the selected photographing mode.

In cases where the range of photographing distance is set at the normal mode, the shortest-distance selecting mode is automatically selected. In cases where the range of photographing distance is set at the far distance mode, the longest-distance selecting mode is automatically selected. As the subject at the longest distance is selected for the final focusing position from among a plurality of image areas without the shortest distance in the range of photographing distance set by the long-distance mode being erroneously selected as the final focusing position, pictures can be taken as desired by the photographer.

In cases where the configuration of the device permits mode selection between the long-range priority mode and the short-range priority mode from within the entire range of photographing distance, it is sufficient for the photographer to simply choose the long-range priority mode; there is no need of complicated operation by the photographer to visually determine the photographing range (for example, whether the subject is in the macro range or the normal range) beforehand. Together with accurate focusing that calls for determining the final focal length after evaluating the reliability of the data, the embodiment enables accurately focused photography that meets the photographer's intention.

Furthermore, the use of the long-range priority mode also

enables accurate focusing to a far distance other than the infinity.

As the method described above calls for calculating and evaluating the distance to the subject in each one of plural areas, it prevents failure in focusing even if the subject has moved or background blur has occurred. Furthermore, even under severe conditions that impair accurate evaluation of the focusing positions, such as when range finding is impossible because contrast evaluated values are too low in all the image areas to produce valid focusing positions, pictures can be taken as desired by the photographer by designating a given distance as the focusing distance based on the photographing mode.

As the present embodiment calls for meeting the photographer's intention, which has been made clear by the selection between short-range priority and long-range priority, the embodiment enables the intuitive confirmation of the focal length prior to an actual photographing action without using complicated algorithms and eliminates the necessity of a special device, such as an optical finder of a single-lens reflex camera or a device that uses a calculation component and serves for enlarged display on an LCD panel. Therefore, compared with a conventional device including a mechanism that permits the camera to automatically recognize the focal length

in an image by using a learning function as well as the selection between short-range priority and long-range priority in order to determine the focal length, the embodiment offers a device having a simplified structure at reduced production costs.

The driving range of the lens varies with respect to the range of photographing distance for which the lens is designed, depending on fluctuation resulting from the lens magnification, a change resulting from a change in aperture, as well as temperature, position and other conditions of the lens barrel, which supports the lens. Therefore, taking into consideration the degree of change resulting from changes in these various conditions in addition to the driving range calculated from the range within which the lens is designed to be focused, the optical system 11 is provided with overstroke ranges at the short-range end and the long-range end respectively. An overstroke range is a range in which the lens is permitted to move by the distance corresponding to the degree of change. Furthermore, the control means, which is comprised of the CPU 17 or the like, is adapted to be capable of driving the lens position of the focus lens unit into an overstroke area.

With the structure as above, in the longest-distance selected mode, even if the in-focus position is near the long-range end of the lens driving range and the lens barrel is oriented towards the far distance side, the range of

photographing distance is ensured by driving the lens of the focus lens unit into the overstroke area at the long-distance end.

Furthermore, in the shortest-distance selected mode, even if the in-focus position is near the short-range end of the lens driving range and the lens barrel is oriented towards the shortest distance side, the range of photographing distance is ensured by driving the lens of the focus lens unit into the overstroke area at the short-distance end.

As described above, the embodiment enables the photography with possible deviation of the focal point occurring near the short-range end or long-range end taken into consideration, thereby easily ensuring the range of photographing distance without the need for a means of control, mechanical or software, for high precision distance correction. Therefore, the embodiment enables reduced production costs.

According to the present embodiment, the photographer may freely set the range of photographing distance and select the long-range priority mode. However, the structure and operation of the device may be simplified by a constitution that permits only one of the two types of selection, i.e. selection of the range of photographing distance or selection of the long-range priority mode.

As described above, according to a method of detecting

a focal length of the present embodiment, the focal length is selected from among the partial focal lengths in the image detecting areas, either the partial focal length at the shortest distance or the partial focal length at the longest distance, in accordance with the operator's choice. The method having this feature enables the selection of an accurate focal length between the shortest focal length and the longest focal length, in accordance with the intention of the operator.

According to a method of detecting a focal length of the present embodiment, a control means selects as the focal length either the partial focal length at the shortest distance or the partial focal length at the longest distance from among the partial focal lengths in the image detecting areas in accordance with the operator's selection of the range of photographing distance. As the control means selects as the focal length either the partial focal length at the shortest distance or the partial focal length at the longest distance from among the partial focal lengths in the image detecting areas in accordance with the operator's selection of the range of photographing distance, the method having this feature enables the selection of an accurate focal length in accordance with the intention of the operator.

According to a method of detecting a focal length of the present embodiment, the focal length is selected based on the

reliability between a partial focal length selected from among the partial focal lengths in the image detecting areas and a given focal length. The method having this feature is based on a method of selecting a focal length from partial focal lengths having a high reliability, and enables the selection of an accurate focal length. Should there be no partial focal length having a high reliability or all the partial focal lengths have a low reliability, a preset focal length is used so as to prevent selection of an inaccurate focal length.

According to a method of detecting a focal length of the present embodiment, the focal length is selected, based on the reliability, between a partial focal length selected from among the partial focal lengths in the image detecting areas and a given focal length that has been set as a result of the operator's choice. The method having this feature is based on a method of selecting a focal length from partial focal lengths having a high reliability, and enables the selection of an accurate focal length between the short distance and the far distance in accordance with the intention of the operator. Should there be no partial focal length having a high reliability or all the partial focal lengths have a low reliability, a preset focal length that corresponds to the operator's choice is used so as to prevent selection of an inaccurate focal length, while reflecting the intention of the operator.

A focusing device according to the present embodiment is provided with a photographing mode selecting means adapted to make selection between a short-distance priority mode and a long-distance priority mode, and the image processing means of the focusing device is adapted to select the focal length with priority given to either the partial focal length at the shortest distance or the partial focal length at the longest distance in accordance with the result of operation of the photographing mode selecting means. The device having this feature enables the selection of an accurate focal length between the short distance and the far distance, in accordance with the intention of the operator. As the device is capable of performing this function without complicating its structure, production costs can be kept under control.

A focusing device according to the present embodiment has an optical system driving means that is capable of driving the optical system into an overstroke range, which is a range beyond the range of focal length for which the optical system is designed. The device having this feature enables easy and accurate focusing at a short distance or a far distance regardless of deviation of the focal point of the optical system resulting from temperature, orientation of the optical system or other conditions.

An image capturing apparatus according to another

embodiment of the invention is explained hereunder, referring to Figs. 17 through 19.

While being based on the constitution described above, the present embodiment involves focus bracket photography, which calls for the photographer to use color data of a plurality of colors generated from image data for calculation of different partial focal lengths for respective color data and take pictures at the respective calculated partial focal lengths. As a prerequisite, bracket photography according to the present embodiment includes the following steps or processes in selection of the photographing modes (Step 11) shown in Fig. 12: calculation of partial focal lengths by using color data within the scope that corresponds to the range of photographing distance selected in Step 1201, selection of the photographing modes (Step 1310) included in image signal determining processing shown in Fig. 13, and various control processes, such as control of whether or which of the auxiliary light sources L1, L2 to be caused to emit light and employing a combination of a plurality of photographing modes.

First, S1 sequence, which is a sequence for photographing a still image, is explained, referring to a flow chart shown in Fig. 17. In the S1 sequence, the shutter button is in a half-depressed state. First, judgment is made as to whether the photographer has already made selection of bracket

photography (Step 1701). In cases where bracket photography has been selected, the variable BL_FLG is set at 1 (BL_FLG=1) (Step 1702). In cases where bracket photography has not been selected, the variable BL FLG is set at 0 (BL_FLG=0) (Step 1703). The variable BL_FLG is used for determining in a later step whether or not bracket photography is going to be performed. Then, exposure processing is performed (Step 1704). The objective of the exposure processing is to determine control criteria to achieve appropriate exposure with regard to a subject. The exposure processing primarily consists of setting the shutter speed, the aperture and the gain of the CCD 12 which serves as an image pickup device.

Next, focusing processing is performed (Step 1705). First, details of focusing processing to be performed in cases where use of auxiliary light has not been set is explained in detail, referring to primarily Fig. 18. In Fig. 18, the process from Step 11 to Step 106 is conducted in the same manner as that shown in Fig. 11. In Step 111 for calculating reliability of each window, the amount of the weight Window(Wh) (CNB) to be placed on the reliability of each color data is calculated (Step 322) as shown in Fig. 15. After the process in Steps 112-114 shown in Fig. 18 is completed, weighting calculation for the evaluated value of each color data is performed (Step 115) in the same manner as the process shown in Fig. 7. Then, after

the process in Steps 116-120, focusing distance calculation is performed based on the calculated evaluated values (Step 121). If the result of focusing distance determination is OK (Step 122), the current state of the focal length, i.e. the focus lens position $P(CNB)$, is stored (Step 125). If the result of focusing distance determination is NG (Step 122), a given focal length which has been set beforehand, i.e. a preset focus lens position $P(CNB)$, is stored (Step 126). CNB mentioned above represents the number of color data items. For example, in cases where three colors consisting of R (red), B (blue) and G (green) are used, CNB is set as 3 so that three focal lengths are calculated. When calculation of all the focal lengths is completed (Step 127), the processing returns to the flow chart shown in Fig. 17. In other words, when the focusing processing (Step 1705) described above is completed, the focus lens position corresponding to each respective color data has been calculated.

In cases where the variable BL_FLG is 0 (Step 1706) in the flow chart shown in Fig. 17, the procedure shifts to determination as to whether actual photography should be performed (Step 1711). In cases where the variable BL_FLG is 1 (Step 1706), the calculated focus lens positions $P(CNB)$ are rearranged sequentially from the shortest focal length (Step 1707), and the lens of the optical system 11 is moved to the

closest focus lens position $P(CNB)$ (Step 1708). In other words, the lens is moved to an end of the linking range as the initial setting in order to perform photographing in succession at a plurality of focus lens positions $P(CNB)$. Therefore, although the calculated focus lens positions $P(CNB)$ are rearranged sequentially from the shortest focal length so that images are photographed in sequence from the shortest focal length, the calculated focus lens positions $P(CNB)$ may be rearranged sequentially from the longest focal length to photograph images in sequence from the farthest distance.

As the next step in the focusing processing in Step 1705, whether or not use of auxiliary light has been selected (See Step 1311 in Fig. 13) is determined by the auxiliary light determining means or the like (Step 1709). In cases where a single auxiliary light source is going to be used (Step 1710), the procedure shifts to whether or not to photograph (Step 1711). In cases where a plurality of auxiliary light sources are going to be used (Step 1710), focusing processing is performed for every combination of the auxiliary light sources to be used so as to calculate each respective focus lens position $P(CNB)$ (Step 1710).

After the lens movement described above, the shutter button is depressed so that, in cases where still-image photography is enabled (Step 1711), photographing processing

(Step 1712) is initiated. The system is at a standstill until the photographing processing is completed (Step 1713). After the photographing processing is completed, judgment is made as to whether a specified number of images has been photographed (Step 1714).

In cases where a single auxiliary light source is used, the number of images taken by bracket photography is CNB. Should it be found in Step 1714 that photographing of a specified number of images has not been completed, the specified number on a counter is reduced by one (-1) (Step 1716). Thereafter, the lens is moved to a focus lens position P(CNB) for a location farther than that for the current lens position (Step 1717). Thus, until the specified number (CNB) of frames of photographs are taken, lens moving and photographing actions are repeated (Steps 1711-1717).

It is thus possible to perform bracket photography, which refers to successive photographing actions at different focal lengths, can be performed by using the partial focal lengths for the image detecting areas obtained for each color data.

The S1 sequence described above is primarily for conducting exposure processing (Step 1707) and focusing processing (Step 1708) in a sequence throughout which the shutter button is in the half-depressed state. In the state where the shutter button is fully depressed (Step 1711),

photographing processing (Step 1712), i.e. an actual bracket photographing action to take still images, is performed (Step 1712). When the shutter button is not in the fully-depressed state (Step 1711) or the specified number of images have been photographed (Step 1715), the S1 sequence is terminated (Step 1715).

Although it is not shown in the drawings, in cases where the S1 sequence has been terminated and the shutter button is in the half-depressed state, the data on the focus lens positions P(CNB) is maintained until the shutter button is fully depressed again. Therefore, bracket photography can be performed by depressing the shutter button further to the fully-depressed position.

In cases where still-image photography was not enabled in Step 1711, the lens is set at a given position which is appropriate for the photographing mode and selected from among the focal lengths calculated for the respective color data.

When the photographing processing (Step 1712) for bracket photography is initiated, a warning is displayed on the image display unit 21 indicating the initiation of bracket photography. This warning may be displayed until the first photographing processing is completed (Step 1713) or until the entire S1 sequence is completed (Step 1713). By thus notifying the photographer that bracket photography is taking place, the

photographer is prevented from moving the image capturing apparatus 10 away from the subject during a photographing action. Although it is not shown in the drawings, the image capturing apparatus 10 may be provided with an audio means, such as speakers, so as to sound a warning at the same moment as the displayed alert. Such an audio warning may be employed together with or instead of a warning display.

As described above, by performing bracket photography at optimum focusing positions for respective color signals, in other words by means of a focusing device that enables bracket photography at optimum focusing positions for respective color signals, which have been obtained by applying weighting calculation to the contrast evaluated values of the respective color data contained in the signals representing each image, the present embodiment increases the possibility of capturing an image for which the lens is correctly focused for a subject on which the photographer intends to focus.

To be more specific, the present embodiment offers calculation processing which includes a means to detect contrast values of respective image data, i.e. image signals, obtained through at least two different color filters (See the matrix complementary circuit 27) and has a function of performing focusing processing for each one of these image signals in the same manner as in the case of the constitution

described above and shown in Figs. 1 through 16. The calculation processing further includes a means to make selection from among said image signals and apply calculation processing to the selected image signal(s) (See the matrix complementary circuit 27, the switch 28 and the Step 12 in Fig. 18) as well as a means to have the lens focus on a subject by applying weighting calculation to the evaluated values of the respective image data obtained by the aforementioned means to perform selection and calculation. The present embodiment also includes a bracket photographing mode (See Fig. 17, which comprises steps of setting a plurality of image detecting areas in each one of the multiple image data, calculating the amount of the weight of reliability of each evaluated value that has been obtained for each image detecting area (See Steps 319-322 in Fig. 15), selecting a given focal length for each output color data from among partial focal lengths in each respective image detecting area based on the evaluated values (See Step 115 in Fig. 7 and Step 115 in Fig. 18) of the partial focal lengths and the employed photographing mode (See Step 11 in Fig. 18), storing distance information for the color data of each respective color (See Steps 125 and 126 in Fig. 18), and taking a plurality of photographs sequentially at the respective partial focal lengths.

By thus including a means to calculate given focal lengths

that are appropriate for the photographing mode from partial focal lengths calculated for the respective image data generated from the data of the initial photographed image (See Step 12 in Fig. 18) and to take photographs sequentially at the calculated focal lengths respectively, the present embodiment enables photography at a focusing position appropriate for features of the subject without having to be concerned with possible deviation of the focal point resulting from a minute difference in colors of the subject.

In other words, in a method or a device for calculating a plurality of focal lengths by using a plurality of image detecting areas and deciding the final focal length from among the calculated focal lengths, partial focal lengths are calculated from multiple image data containing information of different colors. Therefore, by calculating the optimum partial focal lengths for the respective color image data and performing bracket photography based on these partial focal lengths, the present embodiment enables the photographer to obtain an optimum image with a single photographing. According to the present embodiment, whereas the manual mode makes it possible to give evaluated values different weights based on color data of different colors, thereby enabling bracket photography performed exactly as the photographer desires by means of setting of the photographing mode or other criteria,

the automatic mode makes it possible to determine characteristics of the color data of the subject by automatically confirming white balance, color data of light emitted from auxiliary light sources, etc., and apply weighting to evaluated values accordingly so as to achieve easy and accurate focusing.

When using a conventional focusing device which uses only one type of data, i.e. brightness data or color data of a single color, there may be occasions where the device is unable to detect contrast even if the contrast is recognizable to the human eye because of color data. Such a failure in recognition of contrast often occurs when the parts of the patterns that constitute the subject to be photographed have the same brightness. In the case of the present embodiment, however, particularly in low-light condition or when movement of the subject or camera shake is occurring, the aforementioned use of multiple image data containing information of different colors enables the photographer to take a series of photographs with a single photographing action at the optimum partial focal lengths for the respective color data. Therefore, even if the photographer does not have sufficient knowledge of color data, it is possible to photograph an accurately focused subject for which focusing had been difficult for a conventional AF device.

When taking a picture that includes, for example, a flower,

should the photographer wishing to focus on the petals of a flower use only brightness data in the evaluation process, this may cause green leaves surrounding the flower to be erroneously detected as a peak of evaluated values, resulting in a failure to focus on the flower petals. The present embodiment is free from such a problem because partial focal lengths can be calculated from more appropriate data, such as color data; for example, photographing can be performed by focusing on flower petals of a specific color by detecting the partial focal length for the color data corresponding to the color of the flower petals. Furthermore, should there be flowers of different colors, images that include an optimally focused image can be captured by taking a series of photographs focused on the flower petals of the respective flowers with a single photographing action.

Furthermore, it is possible to prevent the photographer from moving the image capturing apparatus 10 in the course of bracket photography by providing the image capturing apparatus with a warning means for notifying the photographer that bracket photography is taking place during or at the beginning of bracket photography. The warning means may use the image display unit 21 to visually display that bracket photography is underway or, either instead of or together with the visual display, use an audio means (not shown) to indicate bracket

photography operation by voice or other sound.

Although the explanation of the embodiment shown in Fig. 17 pertains only to whether or not auxiliary light is used as a photographing, the invention is not limited to such a constitution; it is also possible to provide a bracket photography mode which permits selection of a plurality of photographing modes (See Step 11 in Fig. 12) and take a series of photographs in each photographing mode at a plurality of partial focal lengths based on contrast evaluated values of multiple image data respectively obtained from information of different colors.

For example, instead of auxiliary light processing shown in Steps 1709,1710 in Fig. 17, procedures in Steps 1709,1710 shown in Fig. 19 may be followed. To be more specific, after the calculated focus lens positions $P(CNB)$ are rearranged sequentially from the shortest focal length (Step 1707) and the lens of the optical system 11 is moved to the closest focus lens position $P(CNB)$ (Step 1708), confirmation is made (Step 1709) as to the photographing mode(s) to be employed (See Step 1310 in Fig. 13) in the focusing processing in Step 1705. In cases where a single photographing mode is going to be used (Step 1710), the procedure shifts to determination of photographing (Step 1711). In cases where a plurality of photographing modes are going to be used (Step 1710), focusing processing is performed

for each one of the photographing modes to be used so as to calculate each respective focus lens position $P(CNB)$ (Step 1710).

In the same manner as in the processes shown in Fig. 17, after the lens movement described above, the shutter button is depressed so that, in cases where still-image photography has been enabled (Step 1711), photographing processing (Step 1712) is initiated. The system is at a standstill until the photographing processing is completed (Step 1713). After the photographing processing is completed, judgment is made as to whether a specified number of images have been photographed (Step 1714).

In cases where a single auxiliary light source is used, the number of images taken by the bracket photography is CNB. Should it be found in Step 1714 that photographing of a specified number of images has not been completed, the specified number on a counter is reduced by one (-1) (Step 1716). Thereafter, the lens is moved to a focus lens position $P(CNB)$ for a location farther than that for the current lens position (Step 1717). Thus, until the specified number (CNB) of frames of photographs are taken, lens moving and photographing actions are repeated (Steps 1711-1717).

It is thus possible to perform bracket photography, which refers to successive photographing actions at different focal

lengths, can be performed by using the partial focal lengths for the image detecting areas obtained for each color data.

The present invention is applicable to various image capturing apparatuses, including, but not limited to, digital cameras and video cameras.

Having described preferred embodiments of the invention with reference to the accompanying drawings, it is to be understood that the invention is not limited to those precise embodiments, and that various changes and modifications may be effected therein by one skilled in the art without departing from the scope or spirit of the invention as defined in the appended claims.